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# PRACTICAL CHEMISTRY,

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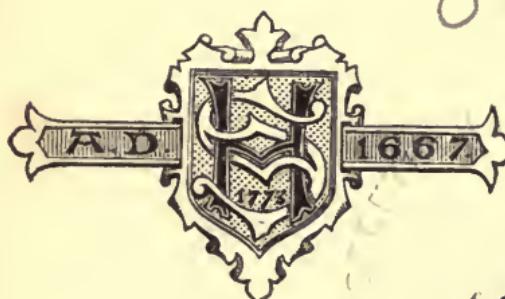
LONDON:  
WILSON and OGILVY,  
Skinner Street.

A COURSE  
OF  
PRACTICAL CHEMISTRY,  
ARRANGED FOR THE  
Use of Medical Students.

BY  
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OF SCIENCES.

Experimenta magis quam præcepta.



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LONDON:

SAMUEL HIGHLEY, 32, FLEET STREET.

1854.



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## P R E F A C E.

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THE following pages contain an outline of the course of practical chemistry annually carried out in the laboratory of Guy's Hospital.

The book consists principally of directions *what* to do : explanations, and details concerning manipulation, are left as much as possible to the oral demonstration of the teacher.

The experiments are arranged in that order which, from his own experience, the author has found best adapted to the wants of the medical student, who, by pursuing the course prescribed, will not only become practised in many of the most important operations of chemistry, but will at the same time acquire a very considerable amount of professional information.

Nearly all the experiments herein described have been

performed during the last three months by the students forming the author's class.

To his former teacher and present colleague, Dr. Alfred Taylor, the writer is under great obligations, as well for his kindness in revising these sheets, as for various suggestions in the application of tests,—more particularly in the toxicological portion of the work.

Should this little book have the good fortune to be adopted in other medical schools, the author will receive thankfully any hints with which the teachers may favour him.

Kennington Road :

August 1st, 1854.

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## APPARATUS

NECESSARY FOR THE PERFORMANCE OF THE COURSE.

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Two dozen Test Tubes.	Two Beakers.
Japanned Blowpipe.	Two Glass Rods.
Washing Bottle.	Three Watch Glasses.
Two Funnels.	Two Files.
Two Porcelain Crucibles.	Spatula.
Two Porcelain Dishes.	Four Strips of Glass.
Water Bath.	Test Tube Stand.
Spirit Lamp.	Florence Flask.
Mortar and Pestle.	Iron Spoon.
Crucible Tongs.	Iron Sand Bath.
Platinum Wire and Foil.	Retort Stand.
Test Tube Cleaner.	Wire Triangle.
Sulph. Hydrogen Apparatus.	200 Circular Filters.
Test Paper.	Two Hard Glass Flasks.
Vulcanised Rubber Tubing.	$\frac{1}{4}$ lb. German Tubing.

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Messrs. Simpson and Maule, 1 and 2, Kennington Road, supply the above Set of Apparatus, in packing case, complete, for 21s.

# GENERAL TESTING.

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## INTRODUCTION.

THE object of the first part of the course is to make the student practically acquainted with the chemical properties of such bodies as are of the most importance, and of the most frequent occurrence.

Of all chemical compounds, those known as *salts* will most frequently present themselves to his notice.

Sulphate of soda and chloride of sodium may be taken as the types of simple salts. The *sulphuric acid* and the *chlorine* are termed the electro-negative or acid constituents; the *soda* and *sodium* the electro-positive or basic constituents, or more simply the bases.

In testing the substances distributed for examination, the student will first of all confine himself to the bases; subsequently he will examine both for bases and acids.

The bases are divided into three great groups, as follows:—

I.	II.	III.
AMMONIA.	ALUMINA.	SILVER.
SODA.	ZINC.	MERCURY.
POTASSA.	CHROME.	LEAD.
MAGNESIA.	NICKEL.	BISMUTH.
LIME.	COBALT.	COPPER.
STRONTIA.	MANGANESE.	CADMIUM.
BARYTA.	IRON.	ANTIMONY.
		TIN.
		ARSENIC.

The members of the third group are precipitated from their acid solutions by hydrosulphuric acid. The members of the second group are *not* precipitated from their acid solutions by hydrosulphuric acid, but are precipitated from their neutral solutions by sulphide of ammonium. The members of the first group are precipitated *neither* by hydrosulphuric acid *nor* by sulphide of ammonium.

Each of the salts presented for examination should contain but one of these basic substances ; and at first the selection should be limited to members of the first group.

By proceeding according to the directions of the Tables appended to each successive group, the student will readily discover the base with which he is dealing. He must then refer to the description of that base, and see how far his substance coincides in its properties with those which are there described ; the simple discovery of the base not being of so much importance as this verification of its properties.

In reply to the question, What is the test for such and such a substance ? the student will have to quote that particular reaction which is alluded to as its special test. Before applying his tests, however, he will generally have to make a solution of his substance ; for this purpose he will proceed according to the succeeding directions.

### SOLUTION OF BODIES.

As a rule, the substance to be dissolved ought to be in a state of fine division ; therefore, pulverise if necessary.

#### 1.

Put a portion of the powder into a test-tube, add a moderate quantity of distilled water, agitate the whole, and heat over a spirit- or gas-flame ; while heating, give the tube an occasional jerk, to facilitate mixture and to avoid the sudden escape of vapour.

If the substance by this treatment is obviously dissolved, filter

if necessary from any insoluble portions, and apply the tests to the clear solution thus formed ; if the substance, however, is not obviously dissolved, filter a few drops on to a glass plate, and gently evaporate them to dryness : should any definite amount of residue remain on the glass, throw the whole mixture upon a filter, and apply the tests to the clear filtrate. There are many substances which do not disappear perceptibly when boiled with water, but yet are sufficiently soluble to afford an aqueous solution that can be successfully tested.

## 2.

Should a mere trace of residue, or none at all, be left upon the glass plate, pour away from the insoluble substance as much as possible of the water, and replace it, little by little, with hydrochloric acid, warming between each addition. Should any obvious action occur, add (if necessary) more of the hydrochloric acid, and heat for some time, until an available solution is formed. Should there be no obvious action, add nitric acid, in the proportion of about one-third of the hydrochloric acid previously employed, and heat. By one or other of these means, a solution will be generally effected—there are indeed a few substances which will dissolve in nitric, but neither in hydrochloric nor in nitro-hydrochloric acid : there are also some substances which are quite insoluble in any of the ordinary menstrua : the consideration of these bodies is however deferred for the present.

The acid solution should generally be diluted with water, unless this dilution produces a precipitate, (in which case the presence of *bismuth* or *antimony* may be suspected) ; the great excess of acid may be partially neutralised with ammonia, if necessary.

## DIRECTIONS FOR TESTING.

Always add re-agents and solvents gradually (unless specially directed to the contrary). This rule is of great importance,

and applies equally to the formation and solution of precipitates : in the latter case agitate between each addition of the solvent.

When directed to employ an excess of any particular reagent or solvent, recollect that every *minute* quantity, more than sufficient to produce the desired effect, is an excess.

In the tables, the solution of the substance in water or acid, to which no reagent has been added, is called the *original solution* : the word *dissolved*, placed at the head of a column, signifies, either that the substances written under it have not been precipitated at all, or that having been precipitated, they are now redissolved by an excess of the reagent,—in any case that they remain in solution.

Proceed with the solution according to the directions of the tables, so as to discover the base ; then turn to the description of the base, and ascertain if the substance under examination possesses the chemical properties which that base is said to possess.

*Note.*—Reduction-tubes are simply pieces of glass-tubing sealed at one end ; they should be about three inches long, and the diameter of the bore should be about three-sixteenths of an inch ; the glass should be clear, moderately thin, and difficultly fusible.

## ERRATA.

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<i>Page.</i>	<i>Line.</i>	<i>Error.</i>	<i>Correction.</i>
28	7	treated	heated.
52	4 b.	found	formed.
90	9	disappear	reappear.
90	8 b.	dissolved by hydrochloric...	undissolved by hydrochloric.
94	16 b.	carbonate of soda	urate of soda.
102	12 b.	1028	1028.

The student is recommended to make these corrections with his pen.



## FIRST GROUP OF BASES.

TABLE I.

Examination of a Solution containing some one Member of the First Group of Bases; namely, AMMONIA, SODA, POTASSA, MAGNESIA, LIME, STRONTIA, BARYTA.

Add Chloride of Ammonium and Carbonate of Ammonia to the original solution, and warm gently.

<i>Precipitated.</i>	<i>Dissolved.</i>	<i>Precipitated.</i>	<i>Dissolved.</i>
BARYTA. STRONTIA. LIME.	MAGNESIA. POTASSA. SODA. AMMONIA.		
Add Sulphate of Potassa to the original solution.	Add Phosphate of Ammonia to the above solution already containing the Ammoniacal Salts, and stir.		
<i>Precipitated.</i>	<i>Dissolved.</i>	<i>Precipitated.</i>	<i>Dissolved.</i>
BARYTA ( <i>quickly</i> ). STRONTIA ( <i>slowly</i> ).	LIME.	MAGNESIA.	POTASSA. SODA. AMMONIA.
Add Hydrofluosilicic Acid to the original solution.		Add to the original solution Tartaric Acid in excess, and stir.	
<i>Precipitated.</i>	<i>Dissolved.</i>	<i>Precipitated.</i>	<i>Dissolved.</i>
BARYTA (in a gelatinous condition).	STRONTIA	POTASSA. AMMONIA ?	SODA. AMMONIA ?

## POTASSA.

1.

All simple potassa salts are soluble in water excepting the bitartrate.

2.

Potassa salts, when heated before the blowpipe, impart to the flame a more or less marked violet colour.

3.

All potassa salts, when heated on platinum foil, leave a fixed and generally fusible residue.

4.

Tartaric acid, when added in excess to a neutral or alkaline solution of a potassa salt, throws down a white crystalline precipitate—bitartrate of potassa. The precipitate frequently does not appear immediately: its deposition is facilitated by stirring the mixed liquids, and by the addition of a little alcohol to them. The precipitate is soluble in mineral acids, in hot water, and in a large excess of cold water.

5.

Bichloride of platinum, when added to neutral or acid solutions of potassa, throws down a yellow crystalline precipitate. It is generally advisable to acidify the potassa solution with hydrochloric acid before adding the reagent. The precipitate does not always appear immediately: its formation is facilitated by stirring, and by the addition of a little alcohol.

The reactions 2, 3, and 5 constitute the special tests for potassa.

## SODA.

1.

All simple soda salts are soluble in water.

## 2.

All soda salts, when heated before the blowpipe, impart an intense yellow colour to the flame.

## 3.

All soda salts, when heated on platinum foil, leave a fixed residue, almost always fusible.

The reaction No. 2 constitutes the special test for soda.

## AMMONIA.

## 1.

All simple ammoniacal salts are soluble in water, excepting the bitartrate.

## 2.

When any ammoniacal salt is boiled with potash or lime, ammoniacal vapour is given off, which is recognised by its smell, by its action on test-paper, and by its forming opaque fumes when brought into contact with the vapour of hydrochloric acid.

## 3.

All ammoniacal salts are partly volatile, most of them entirely so.

## 4.

Tartaric acid reacts upon ammoniacal, as upon potassa salts : the precipitate produced is, however, more soluble in water, and consequently does not form, unless the ammoniacal solution be moderately concentrated.

## 5.

Bichloride of platinum reacts upon ammoniacal precisely as upon potassa salts.

The reaction No. 2 constitutes the special test for ammonia.

## MAGNESIA.

1.

Magnesia, hydrate of magnesia, carbonate of magnesia, and phosphate of magnesia, are insoluble in water. All magnesian precipitates are soluble in ammoniacal solutions, excepting the phosphate and arseniate.

2.

Sulphate of magnesia and oxalate of magnesia are very soluble in water.

3.

Magnesia salts, when heated on platinum foil, leave a white fixed infusible residue; this, when moistened with solution of nitrate of cobalt, and re-ignited by the blow-pipe flame, assumes a faint pink colour.

4.

When an alkaline phosphate is added to a solution of magnesia, rendered alkaline by ammonia, a white crystalline precipitate is produced—soluble in dilute acids, insoluble in ammonia and ammoniacal salts.

The reaction No. 4 constitutes the special test for magnesia: it is obviously inapplicable in the presence of lime, baryta, and strontia salts, as the phosphates of these bases are likewise insoluble.

## BARYTA, STRONTIA, LIME.

These three bases possess many properties in common.

1.

Their hydrates are all soluble in water, so that the addition of an alkali (if perfectly free from carbonic acid) does not disturb their solutions.

## 2.

The following salts of these bases are insoluble in water :— the oxalates,—the phosphates,—the carbonates (even in the presence of ammonical salts,) and the sulphates, (sulphate of baryta the most insoluble, sulphate of lime the least so).

## 3.

When a baryta or strontia, or lime salt, is ignited on platinum foil, a white fixed residue remains, which is generally infusible.

## 4.

Oxalic acid precipitates neutral solutions of strontia and of lime, but not of baryta unless very concentrated. Baryta is, however, readily precipitated by alkaline oxalates. The precipitates of the oxalates of lime and strontia are insoluble, that of baryta soluble, in excess of oxalic acid.

## 5.

Dilute sulphuric acid or weak solutions of neutral sulphates precipitate baryta and strontia, but not lime unless its solution be very concentrated. Solution of sulphate of lime will not precipitate lime under any circumstances.

## 6.

Hydrofluosilicic acid precipitates baryta salts, but is without action on lime and strontia salts.

## 7.

Strontia salts for the most part impart a marked crimson colour to the blow-pipe or other flame; most baryta salts a yellowish green; most lime salts a yellowish red.

## SPECIAL TESTS FOR BARYTA.

Sulphuric acid and solutions of sulphates, even if very dilute, give with baryta salts a white precipitate insoluble in acids or alkalies.

Hydrofluosilicic acid produces in neutral or acid solutions

of baryta salts, a white gelatinous almost transparent precipitate.

#### SPECIAL TESTS FOR STRONTIA.

The reaction with sulphuric acid and the sulphates is similar to that of baryta, but the precipitate is more soluble in water.

Strontia salts, when moistened with hydrochloric acid, and then heated before the blowpipe, impart a deep crimson colour to the flame.

#### SPECIAL TEST FOR LIME.

Oxalate of ammonia produces in neutral or alkaline solutions of lime, a white precipitate, soluble in nitric and hydrochloric acids; insoluble in ammonia and in oxalic and acetic acids. (The presence of strontia would of course lead to a similar result.)

## SECOND GROUP OF BASES.

THE second group of bases includes ALUMINA, ZINC, CHROME, IRON, NICKEL, COBALT, MANGANESE, all of which bodies are precipitated from their neutral or slightly acid solutions by sulphide of ammonium—a reaction which distinguishes them from the members of the first group, and are not precipitated from their acidulous solutions by hydrosulphuric acid—a reaction which distinguishes them from members of the third group.

*Note.*—There are certain earthy salts which do not dissolve in water, but which are readily soluble in dilute mineral acids (nitric or hydrochloric) without, at the same time, undergoing any decomposition; hence, when such an acid solution is neutralised by ammonia, or by sulphide of ammonium, the salts are reprecipitated in their original condition. These salts are principally the fluoride of calcium—the oxalates of lime, strontia, and baryta—and the phosphates of magnesia, lime, strontia, and baryta; so that, although the alkaline earths strictly belong to the first group, they are occasionally precipitated along with the proper members of the second.

Should sulphide of ammonium produce a precipitate in the solution under examination, the student will proceed according to Table II.; if not, according to Table I. Having discovered the base he will refer to its description as before. The further investigation of the earthy salts, however, may be omitted for the present (*vide p. 41*).

The precipitate produced by sulphide of ammonium varies both in its character and in its appearance. The earthy salts are precipitated as such, alumina and chrome as hydrated oxides, the remainder as sulphides.

The precipitate is white in solutions of zinc, alumina, and the earthy salts; black in solutions of iron, nickel, and cobalt; greenish in solutions of chrome; and buff-coloured in those of manganese.

The student must not, however, attach too much importance to the colour of a precipitate, as it is a quality very liable to be interfered with from accidental circumstances.

TABLE II.

Examination of a Solution containing some one Member of the Second Group of Bases; namely, ALUMINA, ZINC, CHROME, NICKEL, COBALT, MANGANESE, IRON.

Add an excess of Potassa Water to a portion of the original solution. The precipitate at first produced may either remain or be re-dissolved.

<i>Precipitated.</i>	<i>Dissolved.</i>	<i>Precipitated.</i>	<i>Dissolved.</i>
NICKEL. COBALT. MANGANESE. IRON. EARTHY SALTS.	ZINC. ALUMINA. CHROME.	To a fresh portion of the original solution add a small quantity of Nitric Acid, and boil for a few minutes, then add at once an excess of Ammonia.	Boil the Potash Solution for some time.
IRON (red). EARTHY SALTS (white).	NICKEL (blue). COBALT (brownish pink). MANGANESE (colourless, speedily becoming brown and turbid).	CHROME.	ZINC. ALUMINA.
			Add a few drops of Sulphide of Ammonium to the Potash solution.
		Pre- cipitated.	Dissolved.
		ZINC.	ALUMINA

## ALUMINA.

1.

Potash and ammonia, also their carbonates and sulphides, give, with solutions of alumina, a white gelatinous precipitate, which is soluble in excess of potash, but reprecipitated on the addition of chloride of ammonium.

2.

Salts of alumina, when heated on platinum foil, leave a white infusible highly incandescent residue: this, when moistened with solution of cobalt and ignited in the blow-pipe flame, assumes a bright blue colour.

## ZINC.

1.

Caustic alkalies give with zinc salts a white precipitate soluble in excess of the precipitant.

2.

Alkaline carbonates give a white precipitate soluble in solutions of ammoniacal salts, insoluble in excess of the fixed alkaline carbonate. The precipitate produced by sulphide of ammonium is insoluble in any alkaline solution.

3.

Zinc salts mixed with carbonate of soda and heated upon charcoal in the reducing blowpipe flame, deposit upon the charcoal an incrustation, which is yellow when hot, white when cold.

4.

Zinc salts heated on platinum foil leave a fixed residue, which is yellow when hot, white when cold; this, when moistened with solution of cobalt and ignited in the blowpipe flame, assumes a fine green colour. This is the most characteristic test for zinc.

## CHROME.

1.

Solutions of chrome salts are mostly green by reflected, violet by transmitted light.

2.

Potash, ammonia, and sulphide of ammonium, throw down a greenish precipitate from solutions of chrome; the precipitate is slightly soluble in excess of ammonia, more so in excess of potash. In each instance it is reprecipitable by boiling.

3.

If a little borax be melted on the end of a platinum wire a clear colourless bead will be produced. If a particle of a chrome compound be attached to the bead, and heat again applied, the chrome will dissolve in the borax, and the bead become of a fine green colour, permanent in both flames of the blowpipe.

4.

If a chrome compound be fused on platinum foil with a little nitre and carbonate of soda, a yellow mass will be produced, soluble in water, the solution giving a yellow precipitate with acetate of lead. This is the most delicate test for chrome.

## IRON.

There are two classes of iron salts, ferrous or proto-salts, and ferric or per-salts. The proto-salts are rarely ever free from admixture of the per-salts. The reactions are described accordingly.

1.

Sulphide of ammonium gives a black precipitate readily soluble in hydrochloric acid.

## 2.

Iron compounds dissolve in the borax bead, forming a glass, which is of a bottle-green colour in the reducing, and of a yellowish-brown colour in the oxidising flame.

## PROTO-SALTS.

## 1.

Ferrous solutions are generally colourless, or of a pale green colour.

## 2.

Caustic alkalies give a dingy green precipitate, which becomes red upon exposure to the air.

## 3.

Ferrocyanide of potassium gives a pale blue precipitate.

## 4.

Ferricyanide of potassium gives a deep blue precipitate. This constitutes the special test for ferrous salts.

## PER-SALTS.

## 1.

Ferric solutions are generally of a yellow, brown, or red colour.

## 2.

Caustic and carbonated alkalies give a brick-dust red precipitate.

## 3.

Ferrocyanide of potassium gives a deep blue coloured precipitate.

## 4.

Ferricyanide does not produce any precipitate, but gives to the solution a colour which is green or brown according to circumstances.

## 5.

Sulphocyanide of potassium imparts to the ferric solution a deep port-wine colour.

The reactions 3 and 5 constitute the special tests for per-salts of iron.

### MANGANESE.

1.

Manganese solutions are of a faint pink tinge, or altogether colourless.

2.

If to a solution of a manganese salt chloride of ammonium be added, and then an excess of ammonia, a clear colourless solution will be produced, speedily becoming brown and opaque when exposed to the air.

3.

Sulphide of ammonium gives a buff-coloured precipitate, soluble even in acetic acid.

4.

Potash gives a white precipitate, speedily becoming brown.

5.

Compounds of manganese fused upon platinum foil with carbonate of soda and a little nitre, yield a bluish-green fusible mass : for this experiment, a very small quantity of the manganese should be employed.

6.

The borax bead with manganese, is amethyst red in the oxidising, nearly colourless in the reducing, flame.

The reactions 3 and 5 are very characteristic.

### NICKEL.

1.

Solutions of nickel are generally of a green colour.

## 2.

Sulphide of ammonium gives with nickel salts a black precipitate, not soluble in hydrochloric acid until after the addition of a drop or two of nitric acid.

## 3.

Ammonia gives a greenish precipitate, soluble in excess, forming a blue solution, from which the precipitate is reproduced on the addition of potash.

## 4.

The borax bead with nickel is, in the oxidising flame, of a dark sherry colour, but with a tinge of violet; in the reducing flame, purplish grey, and turbid. If a fragment of nitre be added, and the bead again heated in the oxidising flame, a bright purple colour is produced.

The reaction No. 3 is characteristic of nickel.

## COBALT.

## 1.

Cobalt solutions are pink when dilute, blue when concentrated.

## 2.

Sulphide of ammonium gives with cobalt salts a black precipitate, not soluble in hydrochloric acid until after the addition of a few drops of nitric acid.

## 3.

Ammonia in excess gives a brown pink-coloured solution, becoming brown when exposed to the air. Potash gives a blue precipitable, insoluble in excess.

## 4.

Cobalt compounds impart to the borax bead, when heated in either flame of the blowpipe, a beautiful blue colour. This is a very characteristic test.

### THIRD GROUP OF BASES.

THE third group includes SILVER, MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, ANTIMONY, TIN, and ARSENIC, all of which bodies are precipitated from their acid solutions by hydrosulphuric acid gas, or its solution in water; a reaction which distinguishes them from the members of the first and second groups of bases. Should, therefore, hydrosulphuric acid produce a precipitate in an acidified solution, the student will proceed according to Table III. Should it produce no obvious precipitate he will render the solution nearly neutral by ammonia, and then add sulphide of ammonium. Should this reagent produce a precipitate he will proceed according to Table II. If no precipitate be produced by either of the above reagents, he will proceed according to Table I.

Before testing with hydrosulphuric acid, the solution must be acidified: either nitric acid or hydrochloric acid will answer the purpose. Should hydrochloric acid produce a white precipitate, it will indicate the presence of silver, proto-salt of mercury, or lead. These can be distinguished from one another as follows:—

The silver precipitate is soluble in ammonia.

The mercury precipitate is turned black by ammonia.

The lead precipitate (which does not form in dilute solutions) is unaffected by ammonia, but is soluble in boiling water.

Under these circumstances it will be unnecessary for the student to follow the directions of the table.

TABLE III.

Examination of a Solution containing some one Member of the Third Group ; namely, SILVER, MERCURY, LEAD, BISMUTH, COPPER, CADMIUM, ANTIMONY, TIN, and ARSENIC.

Acidify the solution with a few drops of Nitric Acid, and pass into it a current of Hydrosulphuric Acid Gas—a precipitate will be formed—allow the precipitate to subside, pour off the supernatant liquor, and replace it by a solution of Sulphide of Ammonium : warm the whole gently.

If the Precipitated Sulphuret be of  
 TIN (*protosalt*), brown,  
 TIN (*persalt*), yellow,  
 ANTIMONY, orange,  
 ARSENIC, yellow,  
 it will dissolve entirely.

On adding Hydrochloric Acid to the solution thus formed, the Sulphurets of the metals will be reprecipitated

TIN, always yellow.  
 ANTIMONY, orange.  
 ARSENIC, yellow.

Allow the precipitate to subside, pour off the supernatant liquor, wash the precipitate by decantation, and then agitate with Sesquicarbonate of Ammonia.

*Dissolved.*  
 ARSENIC.

*Precipitated.*  
 ANTIMONY.  
 TIN.

If the Precipitated Sulphuret be of  
 SILVER,  
 MERCURY,  
 LEAD,  
 BISMUTH,  
 COPPER,  
 CADMIUM, yellow,  
 it will remain undissolved.

The members of this section may generally be distinguished from one another by adding Potash to a portion of the original solution : in any case a precipitate will be produced.

The LEAD precipitate is white, and soluble in excess of the reagent.

MERCURY (*protosalt*), black, unaffected by ammonia.

MERCURY (*persalt*), yellow, turned white by ammonia.

BISMUTH, white, unaffected by ammonia.

COPPER, blue,  
 CADMIUM, white, } soluble in ammonia.  
 SILVER, brown,

Insoluble in excess of potash.

The action of hydrosulphuric acid upon the different members of this group has been described in the table. The precipitates produced vary much from one another as regards their solubility in the mineral acids; only such of them as have a further practical interest will be again alluded to. Certain of the metals composing this group will be considered more fully under the head of Toxicology.

### SILVER.

#### 1.

Hydrochloric acid gives in solutions of silver salts a white precipitate, insoluble in nitric acid, soluble in ammonia. The colour of the precipitate changes to purple by exposure to light.

#### 2.

Potash gives a brown precipitate insoluble in excess, soluble in ammonia.

#### 3.

Silver compounds, when fused with carbonate of soda, upon a charcoal support, in the reducing flame of the blowpipe, yield a button of a white malleable metal, no incrustation being formed on the charcoal. The reaction No. 1 constitutes the special test for silver.

### LEAD.

#### 1.

In moderately strong solutions hydrochloric acid gives a white crystalline precipitate, soluble in boiling water, unaffected by ammonia, soluble in great excess of potash.

#### 2.

Dilute sulphuric acid, or solutions of sulphates, give a dense white precipitate, insoluble in dilute acids, soluble in strong hydrochloric acid with the aid of heat, soluble in large excess of potash.

3.

Potash gives a white precipitate, soluble in excess.

4.

Lead compounds, when fused with carbonate of soda on charcoal in the reducing blowpipe flame, yield a globule of soft white metal, a yellow or brownish-yellow incrustation being formed on the charcoal.

The black precipitate with hydrosulphuric acid, and the white with sulphuric acid, are sufficient to distinguish lead from any other single base.

### BISMUTH.

1.

Water, when added to moderately concentrated, and not over acid solutions of bismuth salts, causes a dense white precipitate, which does not disappear on the addition of tartaric acid. In order to make a solution of a bismuth salt, a considerable excess of acid is required.

2.

Potash gives a white precipitate insoluble in excess, insoluble in ammonia.

3.

Bismuth compounds, when mixed with carbonate of soda, and heated upon charcoal in the reducing blowpipe flame, yield a brittle metallic globule and a yellow incrustation. The reaction No. 1 is most characteristic of bismuth.

### CADMIUM.

1.

The precipitate produced by hydrosulphuric acid is of a bright yellow colour, disappears readily on the addition of nitric or hydrochloric acid, does not form in very acid solutions, is insoluble in sulphide of ammonium.

## 2.

Caustic alkalies give a white precipitate soluble in excess of ammonia. The precipitate produced by carbonate of ammonia does not disappear in an excess of that reagent.

## 3.

Cadmium compounds, fused with carbonate of soda upon charcoal in the reducing flame, give a reddish-brown incrustation. The reaction No. 1 is very characteristic of cadmium.

## COPPER.

## 1.

Ammonia, or its carbonate, gives a blue precipitate soluble in excess of the reagent, forming a deep blue solution, the transparency of which is not affected by the addition of potash.

## 2.

Potash gives a pale blue precipitate insoluble in excess : by ebullition the colour changes to black.

## 3.

Ferrocyanide of potassium gives a chocolate coloured precipitate soluble in large excess of ammonia, forming a deep blue solution.

## 4.

A piece of clean iron or steel, dipped into an acidulated copper solution, becomes coated with metallic copper.

## 5.

Borax beads, heated with minute particles of copper compounds, become blue or green in the oxidising flame, and nearly colourless or reddish grey in the reducing flame.

The reactions 1 and 4 constitute the special tests for copper.

## MERCURY.

There are two classes of mercury salts : the mercurous and

the mercuric. Certain reactions are common to the two; certain others are distinctive between them.

## 1.

The precipitate produced by an excess of hydrosulphuric acid is black; it is insoluble in sulphide of ammonium, and also in strong hot nitric or muriatic acids taken separately,—readily soluble in a mixture of the two.

## 2.

Protochloride of tin produces at first a white precipitate, which, by adding more of the reagent, becomes grey, and finally black. If the supernatant liquor be poured off from the sediment, and this latter boiled with hydrochloric acid, globules of metallic mercury make their appearance.

## 3.

If a piece of clean copper foil be suspended in a mercury solution, it speedily acquires a silvery metallic coating. If the foil be dried and heated in a reduction tube, globules of metallic mercury sublime, and the copper acquires its natural colour.

## MERCUROUS REACTIONS.

## 1.

Hydrochloric acid produces a white precipitate soluble in boiling nitric acid; turned black by ammonia.

## 2.

Potash and ammonia alike produce a black precipitate.

## MERCURIC SALTS.

## 1.

Ammonia gives a white precipitate.

## 2.

Potash gives a yellow precipitate, turned white on the addition of ammonia or in the presence of an ammoniacal salt.

## 3.

Iodide of potassium added carefully, produces a bright orange-red precipitate, soluble in excess of the reagent, forming a colourless solution.

## ANTIMONY.

## 1.

Hydrosulphuric acid produces an orange-coloured precipitate; soluble in sulphide of ammonium, reprecipitated on the addition of an acid; soluble in hydrochloric acid by the aid of heat, more readily by the addition of a little nitric acid also; insoluble in carbonate of ammonia; converted almost entirely into a white insoluble powder by nitric acid.

## 2.

Water added to certain antimony solutions (not to all) produces a white precipitate, soluble in excess of hydrochloric acid, or of tartaric acid.

## 3.

Antimony compounds, when fused with carbonate of soda on charcoal in the reducing blowpipe flame, yield a button of brittle metal, with an abundant bluish white incrustation. If the heat be prolonged, the metal entirely volatilizes, with the formation of white fumes.

## TIN.

Tin salts are of two kinds : stannous or proto-salts, and stannic or per-salts.

## 1.

When compounds of tin are heated with carbonate of soda and cyanide of potassium upon charcoal, a globule of white malleable metal is produced, with very slight if any incrustation. If this globule be dissolved in hydrochloric acid, the tests for stannous salts can be applied to the solution.

## PROTO-SALTS.

1.

Hydrosulphuric acid produces a brown precipitate, soluble in yellow sulphide of ammonium, reprecipitated yellow by the addition of an acid; converted by boiling nitric acid into a white insoluble powder.

2.

Solution of corrosive sublimate added carefully to stannous solutions, produces a precipitate white at first, but speedily becoming grey, and finally black.

## PER-SALTS.

Hydrosulphuric acid produces a yellow precipitate, soluble in ammonia or sulphide of ammonium, reprecipitated on the addition of an acid; soluble in boiling hydrochloric acid, more readily on the addition of a little nitric also; converted by concentrated nitric acid into a white insoluble powder; insoluble in carbonate of ammonia.

## ARSENIC.

1.

Hydrosulphuric acid produces in acidulated solutions of *arsenious acid*, or of *arsenic acid* after the addition of sulphurous acid, a bright yellow precipitate, soluble in ammonia, carbonate of ammonia, and sulphide of ammonia, reprecipitated by acids; insoluble in boiling hydrochloric acid; entirely and readily soluble in hot nitric acid.

2.

Nitrate of silver produces in neutral or slightly ammoniacal solutions of *arsenious acid* a yellow precipitate, soluble

in nitric acid, soluble in ammonia: from similar solutions of *arsenic acid* the preparation is of a brick dust red colour, soluble in ammonia and in nitric acid.

## 3.

Sulphate of copper produces in neutral or very faintly ammoniacal solutions of *arsenious acid* a green precipitate; in similar solutions of *arsenic acid* a blue precipitate, soluble in nitric acid and in ammonia.

## 4.

If a compound of arsenic be mixed with soda flux, and heated in a reduction tube, a steel-grey coloured ring of reduced metal will condense in its upper or cool part.

## 5.

*Arsenious acid* is converted into *arsenic acid* by boiling with concentrated nitric acid, more readily by the addition of a little hydrochloric acid also. In order to apply the tests the solution must be evaporated to dryness, and the residue redissolved in water. *Arsenic acid* is readily converted into *arsenious acid* by the passage of sulphurous acid through the liquid containing it.

## ACIDS, OR ELECTRONEGATIVE BODIES.

THE student is expected to ascertain the nature of the base as well as of the acid in the substance under his examination.

As a rule it is advisable to commence by examining for the *base*. This having been discovered, the *acid* is then to be sought for. In this search the student will be guided much by his knowledge of the special characters of different compounds : thus, if he has presented to him a substance soluble in water or acids, the basic constituent of which proves to be silver, he will not proceed to test it for hydrochloric acid, because he knows that the chloride of silver is perfectly insoluble in aqueous or acidulous solutions.

A solution of the original substance either in water or in dilute nitric acid will serve for the detection of the acid, according to the plan of Table IV., unless the contrary is expressly stated.

Before proceeding according to the tables, it is always advisable to make the following experiment :—

Ignite a small portion of the substance upon either platinum foil or charcoal ; the results are generally best seen upon the foil, but this becomes speedily destroyed if the substance chances to contain an easily reducible metal.

1. The formation of a *white permanently fusible residue* indicates the probable presence of an alkaline salt, or a chloride of barium, strontium, calcium, or zinc.

2. The *volatilization* of the substance indicates the probable presence of ammonia or mercury salts, or arsenious or oxalic acids.

3. A *white infusible residue* indicates the probable presence of alkaline earths, alumina, or oxide of zinc (the last being yellow while hot). This residue may be treated with nitrate of cobalt, as previously described.

4. A *coloured residue, fusible or infusible*, is left by most of the heavy metallic oxides ; many of these may be satisfac-

torily distinguished from one another by fusion, either with the borax bead, or with carbonate of soda upon charcoal, as previously described.

5. *Charring* indicates the presence of fixed organic matter. Tartaric acid gives out a peculiar smell when burnt.

6. Should the substance *deflagrate with organic matter*, and to ascertain this point a fragment of wood may be treated with it, the presence of nitric or chloric acid is indicated.

Of these six indications the first is the most fallacious. If the above experiment, however, have led to a definite result, the student may endeavour simply to confirm that result, instead of proceeding according to the tables. Otherwise he will make a solution of the substance as usual, examine firstly for the bases, according to the Tables III., II., and I., as before, and then test for the acid, according to Table IV. confirming any result he may arrive at by the *special tests*. If the substance charred when heated on platinum foil, it is preferable to use a solution of the ash, in order to detect bases belonging to the first and second groups.

Should the passage of hydrosulphuric acid gas through the acidulated solution of the substance change the colour of the solution from yellow to green, the presence of *Chromic acid* is indicated.

#### TABLE IV.

##### COURSE FOR THE DETECTION OF THE ACIDS.

###### 1.

Put a portion of the original substance into a test tube, moisten it with water, then add a moderate quantity of hydrochloric acid, and apply heat if necessary. Effervescence indicates the presence of carbonic or hydrosulphuric acids.

CARBONIC ACID is inodorous, does not affect lead paper, renders lime water milky.

HYDROSULPHURIC ACID smells strongly, blackens lead paper, is without action on lime water.

Effervescence from other causes can scarcely be confounded with that produced by either of the above acids.

## 2.

Treat a small portion of the original substance in a test-tube, with concentrated sulphuric acid. Apply heat gradually, (with great caution if the substance deflagrated when heated with organic matter) and observe the effects.

A brown discolouration with crackling detonation, indicates **CHLORIC ACID.**

Brownish pungent vapours not affecting starch-paper—

**NITRIC ACID.** The colour of these vapours is occasionally very slight, until after the addition of a few copper turnings.

Brown vapours turning starch-paper yellow—**HYDROBROMIC ACID.**

Purple vapours turning starch-paper purple—**HYDRIODIC ACID.**

Pungent acid fumes—**ACETIC, HYDROCHLORIC, or FLUORIC ACIDS.** The first two recognised by the smell; the third, by the formation of an opaque white film upon a moistened glass rod brought into contact with the vapour, and by the corrosion of the test-tube.

Transfer the contents of the tube into a capsule, add spirit of wine thereto, and ignite; a marked green flame is indicative of **BORACIC ACID.**

## 3.

To the original solution of the substance, add a few drops of nitrate of baryta: the production of a white precipitate, insoluble in nitric acid, indicates the presence of **SULPHURIC ACID.**

## 4. .

Acidulate the solution of the substance with nitric acid, and then add nitrate of silver: a white precipitate may indicate

A.—**HYDROCHLORIC ACID.**—The silver precipitate is soluble in ammonia—insoluble in boiling concentrated nitric acid. The precipitate produced by **HYDROBROMIC**

**ACID** is not so readily soluble in ammonia, and is of a faintly yellow colour.

B.—**HYDRIODIC ACID.**—The precipitate is of a yellowish colour, insoluble in ammonia—insoluble in boiling concentrated nitric acid.

C.—**HYDROCYANIC ACID.**—The precipitate is soluble in ammonia—soluble in concentrated boiling nitric acid, and when ignited leaves a residue of metallic silver.

### 5.

Should the base of the salt be either potash, or soda, or ammonia, apply the following tests to the original solution. Should any other base be present, prepare a solution as follows: Dissolve the original substance in water, or in as small a quantity as possible of hydrochloric acid, add an excess of carbonate of soda, boil and filter. In either case neutralise if necessary.

A.—Add to a neutral or alkaline solution, chloride of ammonium, ammonia, and a few drops of sulphate of magnesia; stir for some time. A white crystalline precipitate indicates **PHOSPHORIC ACID**.

B.—Add to a neutral or acetic acidulous solution, chloride of calcium. A white precipitate, soluble in hydrochloric—insoluble in acetic acid, indicates **OXALIC ACID**.

C.—If the white precipitate, produced by the addition of chloride of calcium to a neutral solution, is soluble in acetic as well as in hydrochloric acid, the presence of **TARTARIC ACID** is indicated.

D.—If the addition of chloride of calcium to the neutral solution does not cause any well-marked precipitate, agitate briskly, filter if necessary, and boil the liquid for some time. A white precipitate indicates **CITRIC ACID**.

E.—To a neutral solution add sesquichloride of iron. The development of a dark red-coloured-liquid, rendered opaque by ebullition, denotes **ACETIC ACID**.

### 6.

Introduce a small portion of the original substance into a

test-tube, add hydrochloric acid, agitate briskly, warm gently, and filter if necessary ; evaporate the solution to dryness, and heat the residue. Should this residue be insoluble in hydrochloric acid, the presence of **SILICIC ACID** is indicated.

### SPECIAL TESTS FOR THE ACIDS.

#### CHROMIC ACID.

1.

Acetate of lead gives, with solutions of the chromates, a yellow precipitate soluble in nitric acid.

2.

Chromates, when boiled with hydrochloric acid and a little spirits of wine, form a green-coloured solution, to which the tests for chrome can be applied. The reaction with sulphuretted hydrogen has been described.

#### CARBONIC ACID.

When hydrochloric acid is added to a carbonate, effervescence takes place. If the gas be cautiously poured into a test-tube containing lime water or a solution of subacetate of lead, and if the gas and liquid be then agitated together, a white precipitate will be produced.

#### HYDROSULPHURIC ACID.

1.

Most sulphides, when acted upon by hydrochloric acid, especially on the application of heat, evolve hydrosulphuric acid, which is known by its smell, and by the brown or metallic-looking black stain produced on lead-paper. Soluble sulphides give a dense black precipitate with nitrate of silver.

2.

All sulphides when fused with carbonate of soda in a porcelain capsule, leave a residue which disengages hydrosulphuric acid, upon the addition of an acid. If this residue be moistened with water, and placed on a silver coin, a brown-black stain will be produced thereon.

## 3.

Most sulphides, when heated in a glass tube open at both ends, evolve sulphurous acid, which is known by its smell of burning sulphur, and by its producing a purple stain on starch-paper moistened with iodic acid.

## SULPHURIC ACID.

## 1.

The precipitate produced by baryta salts in solutions of the sulphates, is perfectly insoluble in nitric or hydrochloric acid. If the precipitate be dried, ignited with carbonate of soda and charcoal, and if the residue be placed upon a piece of lead-paper, and moistened with dilute hydrochloric acid, a deep-brown stain will be produced upon the paper.

## BORACIC ACID.

## 1.

Baryta salts give a white precipitate, moderately insoluble in water, soluble in solutions of ammoniacal salts, soluble in dilute nitric acid.

## 2.

If the presence of boracic acid is suspected from the colour of the alcohol flame, acidify a solution of the substance with hydrochloric acid, and test with blue litmus and with turmeric papers. If the litmus paper be reddened, at the same time that the turmeric paper is browned, the presence of boracic acid is certain.

## PHOSPHORIC ACID.

## 1.

When chloride of ammonium, ammonia, and sulphate of magnesia, are added to a solution of an alkaline phosphate, a white crystalline precipitate is produced: the precipitate forms most readily when the liquid is agitated with a stirring rod: it is insoluble in ammonia, soluble in acids.

## 2.

When nitrate of silver is added to a neutral or slightly

alkaline solution of phosphoric acid, a yellow (under certain circumstances white) flocculent precipitate is produced, soluble in ammonia and in dilute nitric acid.

## 3.

If a solution containing phosphoric acid be rendered acid with acetic acid (if the solution be acid from the presence of a mineral acid, an alkaline acetate can be used for the purpose), and then a minute drop of sesquichloride of iron be added, the drop will become of a red colour, speedily however changing to a white opaque cloud ; on the addition of more of the reagent, the precipitate will become reddish brown, as also the supernatant liquor ; if the whole be boiled and thrown upon a filter, the filtrate will be colourless, and perfectly free from both iron and phosphoric acid. This mode of testing is applicable in the presence of the alkaline earths, which is not the case with the other two.

## HYDROCHLORIC ACID.

## 1.

Nitrate of silver gives in solutions of hydrochloric acid (chlorides) a dense white precipitate, becoming of a slate colour when exposed to the light : the precipitate is insoluble even in boiling concentrated nitric acid, readily soluble in ammonia ; when heated in a porcelain capsule it does not undergo decomposition, but simply fuses.

## 2.

When chlorides are mixed with binoxide of manganese and sulphuric acid in a test-tube, chlorine gas is given off, which is recognised by its odour and yellowish-green colour, and by its bleaching litmus paper. If a piece of starch-paper, dipped in iodide of potassium solution, be held over the mouth of the tube, a deep purple stain will be produced.

## HYDROBROMIC ACID.

## 1.

The precipitate produced by nitrate of silver resembles that

produced in solutions of the chlorides ; it is, however, faintly yellow in colour, and less readily soluble in ammonia.

## 2.

Bromides, when acted upon by binoxide of manganese and sulphuric acid, evolve bromine, which is recognised by its red-coloured vapours, by its smell, by its imparting a yellow colour to starch-paper, and by its bleaching litmus paper.

## HYDRIODIC ACID.

## 1.

The precipitate produced by nitrate of silver is of a pale yellow colour ; insoluble in, but turned white by, ammonia ; in other respects similar to the chloride.

## 2.

If a solution of an iodide be mixed with starch-water, and a few drops of nitric or nitro-hydrochloric acid be added, a deep blue or purple colour will be produced.

## 3.

Iodides, when acted upon by binoxide of manganese and sulphuric acid, evolve iodine. This is recognised by its purple vapour, which stains starch-paper purple.

## HYDROCYANIC ACID.

## 1.

Nitrate of silver produces a clotty white precipitate, insoluble in cold nitric acid, soluble in concentrated boiling nitric acid, soluble in ammonia. If the precipitate be washed, dried, and ignited in a reduction-tube, cyanogen gas will be given off, and metallic silver remain ; if a light be applied to the mouth of the tube, the cyanogen will burn with its peculiar rose-coloured flame.

## 2.

If to a solution containing hydrocyanic acid, a solution of common green vitriol be added, and then an excess of potash water, a dirty green-coloured precipitate will be produced ; if now an excess of hydrochloric acid be added, part of the precipitate will dissolve, and a bright blue residue (*prussian blue*) remain.

For further details concerning hydrocyanic acid, refer to the Toxicological portion of this work.

### NITRIC ACID.

1.

The nitrates are all soluble salts; they deflagrate when heated with organic matter.

2.

If a solution of a nitrate be mixed gradually with an equal bulk of sulphuric acid, and the whole cooled, and if then a moderately strong cold solution of protosulphate of iron be added cautiously, where the two fluids meet a deep brown halo will be produced.

3.

If a nitrate, or a concentrated solution thereof, be heated with sulphuric acid and a few copper turnings, pungent orange-coloured non-bleaching acid fumes will be evolved.

4.

If a minute quantity of gold-leaf be boiled in hydrochloric acid, no action will take place; but on the addition of nitric acid, or a nitrate, the gold will disappear, and may be detected in the solution by the addition of protochloride of tin, which will give rise to a purplish precipitate.

### CHLORIC ACID.

1.

The chlorates are all soluble salts; they deflagrate when heated with organic matter.

2.

When sulphuric acid is added to a chlorate, crackling detonation occurs, and a brown colour is produced; hydrochloric acid evolves a greenish-yellow gas.

3.

Chlorates give no precipitate with nitrate of silver. If a portion of a chlorate be heated for some time in a test-tube, oxygen gas is given off, known by its inflaming a piece of incandescent wood; and the residue, when dissolved in water,

affords an abundant white clotty precipitate of chloride of silver.

### HYDROFLUORIC ACID.

1.

If a powdered fluoride, placed upon a watch-glass, be moistened with sulphuric acid, and gently heated, dense pungent acid fumes, extremely opaque in moist acid, will be given off, and the surface of the watch-glass will become corroded.

2.

If a mixture of a fluoride with sand, be put into a test-tube, and moistened with sulphuric acid, and if by means of a cork, a narrow piece of tube, moistened on its interior with water, be adapted to the mouth of the test-tube, on the application of heat the narrow tube will receive an opaque lining.

### OXALIC ACID.

1.

This acid differs from most other fixed organic acids, inasmuch as neither it, nor its salts, become charred when acted upon by heat or by sulphuric acid.

2.

Oxalates soluble in water, or oxalates soluble in acid after the addition of acetate of ammonia, give with all lime-salts, even the sulphate, a white precipitate, insoluble in ammonia, insoluble in acetic acid, soluble in dilute mineral acids.

### TARTARIC ACID.

1.

Tartaric acid and the tartrates, when heated, evolve a very peculiar odour, and leave an abundant charcoal.

2.

If to a moderately concentrated solution of tartaric acid, or a tartrate rendered acid with acetic acid, acetate of potash be added, a white crystalline precipitate will be produced, especially on stirring, or on the addition of alcohol: the addition of acetate of potash is unnecessary, if potash or ammonia salts are known to exist in the solution.

## 3.

In neutral solutions of the tartrates, chloride of calcium produces a white precipitate, soluble in acetic acid.

## 4.

In neutral solutions of the tartrates, nitrate of silver produces a white precipitate, which speedily becomes black on boiling.

## 5.

Tartaric acid and tartrates become blackened when heated with sulphuric acid.

## CITRIC ACID.

## 1.

The acid and its salts, when heated on platinum foil, leave an abundant charcoal.

## 2.

Chloride of calcium does not produce any precipitate in neutral citrates until after the application of heat.

## 3.

Nitrate of silver produces in neutral citrates a white precipitate, which becomes of a yellow colour on boiling.

## 4.

Citric acid and citrates do not afford a black, but only a yellow colour, when heated with sulphuric acid.

## ACETIC ACID.

## 1.

When a few drops of perchloride of iron are added to an alkaline acetate, a deep red-coloured liquid is produced ; on ebullition a brick-dust deposit takes place, and the supernatant liquor becomes colourless.

## 2.

When an acetate is heated with sulphuric acid and spirits of wine, acetic ether is developed, which is known by its characteristic odour.

## SUBSTANCES INSOLUBLE IN WATER AND ACIDS.

There are certain substances which will not dissolve in water, nor in any ordinary acid, nor in any combination of acids, even with the aid of heat. Of this class of bodies the following ones are most likely to present themselves to the student :—

1. Tin binoxide.
2. Antimonious acid.
3. Silver chloride, bromide, or iodide.
4. Baryta sulphate.
5. Strontia sulphate.
6. Chrome (*green*).
7. Alumina and aluminates.
8. Silica and silicates.

The substances 3, 4, and 5 are always insoluble in acids ; the others occur sometimes in the soluble, sometimes in the insoluble form. Sulphate of strontia is so soluble in water, that its acid may be precipitated by a barytic salt.

The first six of the above-mentioned insoluble substances may be readily recognised by the following experiments :—

Mix the finely-powdered substance with a little soda flux (a mixture of carbonate of soda with cyanide of potassium is preferable), and using a charcoal support, heat the mixture for some time in the reducing flame of the blowpipe.

*Metallic reduction* will indicate the presence of ANTIMONY, TIN, or SILVER.

ANTIMONY gives rise to an abundant white incrustation upon the charcoal, and forms a brittle globule, which is converted into a white powder by concentrated nitric acid, is insoluble in hydrochloric, soluble in nitro-hydrochloric acid, the solution, if not too acid, being precipitable by water. (See *Reactions of Antimony*.)

TIN does not give rise to any incrustation. The globule is white and malleable, is converted into a white powder by

strong nitric acid, is readily soluble in hydrochloric acid with the aid of heat. The solution gives, with solution of corrosive sublimate, a precipitate white at first, but subsequently black. (See *Reactions of Tin*.)

SILVER does not produce any incrustation. The metal is white and malleable, perfectly soluble in nitric acid, which solution gives with hydrochloric acid a white clotty precipitate soluble in ammonia. If silver be present, boil a portion of the original substance for some time in a solution of potash, dilute and filter. To the filtrate apply the special tests for chlorine, bromine, and iodine.

Should there *not* be any metallic reduction, place a portion of the fused mass upon a piece of lead-paper, and moisten it with a drop of dilute hydrochloric acid; the blackening of the lead-paper will indicate the presence of sulphur derived from the SULPHURIC ACID of the sulphate of baryta or of strontia.

To distinguish between these two, fuse a fresh portion of the original substance with carbonate of soda; boil the fused mass in water, filter, and in the filtrate, test for sulphuric acid. Wash the portion insoluble in water, and dissolve it in a few drops of hydrochloric acid: in this solution, test for BARYTA and STRONTIA, and distinguish between them by the colour of the flame.

CHROME is known by its green colour. After prolonged fusion with carbonate of soda it assumes an altered condition, and becomes soluble in acids. It is preferable, however, to fuse it with nitre in a small porcelain capsule: by this means it becomes converted into chromate of potash, which dissolves very readily in water, and forms a solution to which the tests for chromic acid can be readily applied. The recognition of chrome is, moreover, readily effected by the borax bead.

#### SILICA AND ALUMINA.

The analysis of siliceous and aluminous compounds is occasionally somewhat difficult. Reduce the substance to a very

fine powder, mix it intimately with three or four times its bulk of carbonate of soda, and fuse it for some time in a platinum capsule or on foil; boil the fused mass in water; filter slightly, overneutralise the filtrate with hydrochloric acid, and evaporate down. The production of a white flocculent precipitate will indicate the presence of SILICA, which may be further identified by evaporating the solution, collecting and drying the precipitate, and fusing it upon the end of a platinum wire with a very minute quantity of carbonate of soda, when a colourless transparent bead will result. The portion of the fused mass which did not dissolve in water is to be dissolved in hydrochloric acid and tested for ALUMINA and the bases generally. The detection of the alkalies in the insoluble alkaline silicates cannot be effected in the above manner. Their exact determination is a matter of some little difficulty. A rough mode of testing consists in reducing the silicate to an *extremely fine* powder, and boiling it for some time with hydrochloric acid. On diluting, filtering, evaporating to dryness, and redissolving the residue in water, a solution is procured, which may in general be examined successfully for the alkalies.

### SPECIAL SUBSTANCES.

As it is almost impossible to give general rules that shall apply to every particular case, it remains to mention some few substances, the detection of which, according to the directions of the Tables, is either difficult or liable to fallacy.

#### POTASH SALTS.

**BITARTRATE.**—The preliminary heating on platinum foil will indicate the probable presence of tartaric acid, and if the charred mass be treated with water an alkaline solution will be obtained which will give the reactions of potash. The aqueous solution of the bitartrate cannot of course be precipitated by tartaric acid, but a solution in hydrochloric acid can be readily precipitated by bichloride of platinum. By

boiling the salt in water to which a few drops of potash have been added, a solution not having an alkaline reaction will be obtained, in which the tartaric acid can be detected by the usual tests.

**BISULPHATE.**—This being an acid salt, the potash cannot be precipitated from it by tartaric acid, until after the neutralisation of its solution with carbonate of soda.

### EARTHY SALTS.

Precipitated from their acid solutions by sulphide of ammonium. Add to the acid solution a considerable excess of carbonate of soda, boil, and filter.

Render the filtrate nearly neutral with hydrochloric acid. Test for **OXALIC ACID** with chloride of calcium and acetic acid, and for **PHOSPHORIC ACID** with sulphate of magnesia, chloride of ammonium, and ammonia.

**FLUORINE** would be detected by the student in the preliminary examination of the substance. Fluoride of calcium, the only fluoride likely to present itself to him, is, when finely pulverised, sufficiently soluble in hydrochloric acid to be proceeded with as above described.

Wash the undissolved portion with water, dissolve it in a small quantity of hydrochloric acid, and in the acid solution test for **BARYTA** and **STRONTIA** by sulphate of potash and the blowpipe flame; test for **LIME** by oxalate of ammonia and ammonia; test for **MAGNESIA** by phosphate of ammonia and ammonia.

### MERCURY SALTS.

**CALOMEL** is readily soluble in nitric acid, but in the act of solution becomes converted into a *mercuric* salt. That it was originally a *mercurous* salt, is shown by the powder itself becoming black when agitated with potash water.

**AMIDO-CHLORIDE.**—This, which is a mercuric compound, is readily distinguished from calomel, by heating it gently with potash-water. The powder becomes of an orange-yellow colour, and ammoniacal vapours are given off.

### ARSENIC.

The SULPHURETS are orange-coloured volatile substances which answer well, to the reduction-tests for arsenic. When boiled with nitro-hydrochloric acid, a solution of *arsenic* acid is formed, which solution is not readily precipitable by hydro-sulphuric acid until after the addition of sulphurous acid. By boiling the powder in hydrochloric acid, and adding the nitric acid only drop by drop, not attempting to dissolve the whole of the substance, but diluting with water and pouring off the clear liquid, a solution is procured, which, when the gas has been passed through it for some time, will afford a yellow precipitate.

### SULPHIDES OR SULPHURETS.

Such of the sulphides as are soluble only in nitro-hydro-chloric, or in concentrated nitric acid, become by the action of the acid, converted into sulphates. That the sulphuric acid did not, however, exist in the original substance, is shown by fusing this latter with carbonate of soda. The fused mass, when dissolved in water, will afford the reactions of hydrosulphuric but not of sulphuric acid. Some of these sulphides are extremely difficult to dissolve completely in acid, in consequence of the deposition of sulphur, which fuses around the unaltered substance and prevents the action of the acid upon it.

### OXIDES.

These are generally recognised by their physical properties, and by their not answering to the tests for any of the acids. The peroxides, when boiled with hydrochloric acid, give off chlorine. The soluble oxides are known by their alkalinity to test paper,—by their effervescing not at all, or but very slightly, upon the addition of an acid,—and by their giving a brown precipitate with a solution of nitrate of silver.

# TOXICOLOGICAL CHEMISTRY.

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FOR the performance of this part of the course, the student will have placed before him in succession, each of the most important poisons, in a variety of forms. He is expected to examine the poison in all the conditions in which it may be presented to him, and to verify all its described properties. Of the acid poisons, the principal are the SULPHURIC, NITRIC, HYDROCHLORIC, and OXALIC. Of the metallic poisons, MERCURY, LEAD, COPPER, ARSENIC, and ANTIMONY. Of the organic poisons, OPIUM and PRUSSIC ACID.

The principal forms in which any particular poison may present itself, are—its usual or normal condition ; dissolved in or diluted with water ; in an organic liquid, either the vehicle in which it was administered, or the contents of the stomach ; in the solid tissues ; and as stains upon clothing.

## SULPHURIC ACID.

### CONCENTRATED.

1. Volatility. Heat a few drops cautiously on a watch-glass, or on platinum foil, the acid will disappear entirely, with the formation of opaque white acrid fumes.
2. Charring organic matter. Dip a piece of paper, wood, or sugar, into the acid ; it will speedily become blackened, or carbonised.
3. Evolution of sulphurous acid. Put a few chips of wood, copper cuttings, or mercury, into a test-tube ; pour in a little of the acid, and heat ; a vapour having a peculiar suffocating smell will be evolved. Hold over the mouth of the tube a piece of starch-paper, dipped in iodic acid, the paper will at first be rendered blue, but ultimately bleached.
4. Manifestation of heat. To about a fluid drachm of the acid in a test-tube, add an equal bulk of water, agitate for a minute or so, the heat produced will be insupportable to the hand applied to the bottom of the tube.

## DILUTED.

1. Volatility.
2. Acid reaction to test-paper.
3. Charring organic matter after concentration. Write upon paper with the dilute acid, the characters will simply appear wet; dry the paper over a stove or gas flame, the characters will become gradually black from the carbonization of the paper.
4. Production of a white precipitate of the reagent. Add a few drops, first of nitric acid, and then by the addition will not dissolve sensibly in any amount of water, of nitrate of baryta or chloride of barium.
5. Manifestation of sulphur in the above precipitate. Collect upon a filter, wash and dry the precipitate; mix it intimately with three or four times its bulk of powdered charcoal; heat the mixture in a reduction-tube; place the residue upon a piece of moistened lead-paper, (glazed card,) which will become stained of a brown or black colour, either immediately or upon the addition of a few drops of hydrochloric acid to the incinerated residue.

Note 1.—For certain objections to some of the above tests, as giving similar reactions with the saline sulphates, &c., consult Taylor "On Poisons," page 210.

Note 2.—The reactions of the dilute acid, numbered 2, 3, 4, and 5, are for the most part equally applicable to cases where the acid is contained in some organic liquid, as coffee or beer, &c.; should the liquid however, be thick and viscid, it must previously be diluted with water, then boiled for some time, with or without the addition of a little acetic acid, and filtered through paper or fine muslin.

## IN VOMITED MATTERS, OR IN THE CONTENTS OF THE STOMACH.

Dilute considerably with water, boil for some time, and filter; the filtrate will have an acid reaction, and will give the characteristic precipitate with a barytic salt.

Note 1.—From the administration of antidotes, &c., the vomited matters may not manifest any, or only a very slight, acid reaction.

Note 2.—The precipitate of sulphate of baryta may be derived from sulphuric acid ingested in the free state, and continuing free; or from sulphuric acid ingested in the free state, but subsequently neutralised; or from some neutral sulphate originally ingested as such; or from the minute quantity of sulphates naturally existing in the secretions.

## STAINS ON CLOTHING.

1.—On black cloth: from the concentrated acid a brown stain, with or without a red border; from the diluted acid a red stain, gradually becoming brown. On other dyed articles according to the dye.

2.—In all cases the fibre becomes destroyed with greater or less rapidity.

3.—The stains remain moist for some time.

4.—When the stained pieces are boiled in water, a solution of sulphuric acid is formed, which will manifest acidity to test paper, and give the reactions with nitrate of baryta.

5.—A piece of the stained stuff, heated in a small reduction tube, evolves sulphurous acid ; a piece of starch paper, moistened with iodic acid, and held over the mouth of the tube, is at first turned blue, and ultimately bleached.

### NITRIC ACID.

#### A.—CONCENTRATED.

1. Colour. Nitric acid, when pure, is colourless ; when containing per-oxide of nitrogen, straw yellow or orange, sometimes even green or blue.
2. Evolution of fumes. The concentrated acid, when exposed to the air at ordinary temperatures, gives off colourless or orange fumes.
3. Volatility. Heat a few drops on a watch-glass, no residue will be left.
4. Action on organic matter. Dip a piece of nitrogenised organic matter (as a strip of flannel) into nitric acid, the tissue will be stained distinctly yellow, the colour being rendered darker, and somewhat brown, by the subsequent action of caustic alkali ; black and coloured cloths are likewise stained of a yellow colour, the tissue at the same time becoming corroded.
5. Action on copper, mercury, &c. To a little nitric acid in a test tube add a few copper turnings, or a drop or two of mercury, and apply heat if necessary ; violent chemical action will take place, as evidenced by the solution of the metal, and by the copious evolution of brownish red acid vapours.
6. Action on sulphate of iron. Drop a crystal of sulphate of iron into nitric acid, a dark greenish brown colour will be produced, which will disappear upon the application of heat.
7. Solution of gold. Boil a minute quantity of gold leaf in hydrochloric acid it will remain unchanged, but on the addition of a few drops of nitric acid will disappear.

#### B.—DILUTED.

The dilute acid is volatile ; has an acid reaction ; when evaporated from paper moistened with it, does not leave a black, but only a slightly yellow, stain ; if pure, gives no precipitate with solutions of nitrate of baryta and nitrate of silver respectively ; reacts with sulphate of iron as above described : when neutralised by a solution of a caustic or carbonated alkali, a *nitrate* is formed, which salt may be obtained solid and crystalline by evaporation upon a glass plate.

## C.—NITRATES.

1. Forms of crystallisation. Evaporate a few drops of a solution of a nitrate upon a glass plate, or place a few crushed crystals upon a glass plate, then add a few drops of water, and apply heat cautiously ; as soon as a solid margin appears, set the liquid aside to crystallise ; nitrate of potash crystallises in lengthened prisms (six sided and fluted), nitrate of soda in well marked rhombs ; the crystals may be examined by a pocket lens, or by the low power of a microscope.
2. Deflagration when heated with charcoal, &c. Mix a few powdered crystals of a nitrate with powdered charcoal, and heat the mixture upon platinum foil, deflagration will ensue, and the residue will have a powerfully alkaline reaction ; or immerse a piece of bibulous paper in a solution of a nitrate, dry and ignite it, the deflagration will be very manifest.
3. Action of sulphuric acid. To a small quantity of a solid nitrate in a test tube, add sulphuric acid in sufficient amount to render the whole moist ; a vapour will be gradually evolved, either colourless or slightly reddish brown, acidifying but not bleaching blue test paper, without action on starch paper.
4. Action on copper. This test may be performed on a very small scale ; wrap a minute crystal of the nitrate in a small piece of fine copper gauze, place the pellet in a very small test tube, or even a reduction tube, and let fall upon it a drop or two of sulphuric acid ; orange-red, acid, non-bleaching vapours will be given off ; or a little powdered nitrate may be mixed with Dutch metal, transferred to a tube, and acted upon by sulphuric acid ; or a solution of a nitrate may be heated with finely divided copper and sulphuric acid.
5. Action on sulphate of iron. To a solution of a nitrate add an equal bulk of sulphuric acid, *cool* the mixture, and drop into it a crystal of sulphate of iron ; allow the whole to stand *without* agitation, and after some time a dark greenish-brown colour will be developed around the crystal.
6. Solution of gold. Boil a minute quantity of gold leaf in hydrochloric acid it will remain unchanged. Add a little of the nitrate, and the gold will be dissolved wholly or in part : in the latter case, to demonstrate the solution of the gold, add protochloride of tin, which will give rise to a purplish precipitate or turbidity.

## D.—IN ORGANIC MIXTURES.

If solid, digest in cold water and filter ; if a viscid liquid, dilute and filter ; if a liquid mixed with solid substances, simply filter. Examine the filtrate, or the original liquid, if filtration has not been adopted,

with test paper; if acid, neutralise with carbonate of soda or of potash; decolourise, if requisite, by boiling with animal charcoal; filter, evaporate, and crystallise. (If necessary dissolve the crystals in water, boil again with animal charcoal, filter, evaporate and crystallise.) To the residue apply the above-described tests, for the nitrates particularly the re-action No. 4. This mode of testing is applicable to recent stains on clothing. The acid re-action may be wanting in organic mixtures, through previous neutralisation.

### HYDROCHLORIC ACID.

#### A.—CONCENTRATED.

1. Colour. The pure acid is colourless, or of a very faint green tinge. The commercial acid is of a yellow colour, owing to the presence of iron.
2. Volatility. Heat a few drops on a watch-glass; no residue will be left.
3. Action on organic matter. Most organic substances become gradually corroded and tinged of a yellow colour by immersion in the acid; the stains produced upon black cloth are distinctly red, becoming however brown after some days.
4. Want of action on copper, mercury, &c. Boil a small quantity of either metal, with hydrochloric acid; the acid will simply volatilise, and the metal remain unchanged.
5. Action on bioxide of manganese. Boil some hydrochloric acid with bioxide of manganese in a test tube; chlorine gas will be abundantly evolved; this gas may be recognised by its yellow colour, by its irritating smell, and by its bleaching litmus paper.

#### B.—DILUTED.

1. Acidity.
2. Volatility.
3. White precipitate with nitrate of silver. Add a solution of nitrate of silver to a portion of the acid; a dense clotty white precipitate will be produced; agitate the whole briskly, after which the precipitate will readily subside. Pour off the supernatant liquor and test the precipitate as follows: treat one portion with ammonia, it will dissolve readily; boil another portion with concentrated nitric acid, it will remain unacted upon; treat another portion with *cold* potash water, it will undergo no change in colour; collect the remainder of the precipitate upon a filter, wash, dry, and ignite upon platinum foil, it will fuse into a horny mass; the precipitate, when exposed to the light, from being colourless becomes of a purplish slate colour.

#### C.—IN ORGANIC LIQUIDS.

1. Acidity.
2. Distillation of the acid. Strain or filter a portion of the liquid if necessary, transfer it into a retort, or into a flask to which a cork and delivery tube have been attached,

and apply heat ; if requisite distil to dryness ; the distillate should manifest the characters of the diluted acid.

#### D.—ON SOLID SUBSTANCES.

##### 1. Acidity.

Immerse the substance in distilled water ; should the liquid acquire an acid re-action, apply the nitrate of silver test.

#### OXALIC ACID.

##### A.—IN THE SOLID STATE.

1. Crystalline appearance.
2. Solubility in water.
3. Volatility without charring.

Oxalic acid generally occurs in more or less defined four-sided prisms.

Place a few of the crystals upon a piece of platinum foil, and apply heat, the acid will melt, evolve fumes, and disappear without leaving any carbonaceous residue.

##### B.—IN AQUEOUS SOLUTION.

1. Acidity.
2. Formation of crystals upon evaporation.
3. Bluish-white precipitate, with sulphate of copper.
4. White precipitate with nitrate of silver.
5. White precipitate, with sulphate of lime.

Evaporate a few drops cautiously upon a glass plate. As soon as a white margin appears around the liquid, set it aside to crystallize. With care, delicate needle-like crystals will be produced.

To a portion of the acid solution in a test tube —add a little solution of sulphate of copper : a bluish-white precipitate will be produced.

To a solution of the acid add a few drops of —add a little solution of sulphate of copper : a bluish-white precipitate will be produced.

To a portion of the acid solution add a considerable portion of a solution of sulphate of lime—a white precipitate will be produced, insoluble in acetic, but readily soluble in dilute nitric acid.

##### C.—IN ORGANIC LIQUIDS, VOMITED MATTERS, CONTENTS OF THE STOMACH, &c.

It may be necessary to filter the liquid, or at least to strain it through fine muslin, with or without previous dilution ; or it may be advisable to boil the whole with a portion of distilled water previous to filtration.

1. Acidity.
2. Bluish or greenish To the strained or filtered liquid add a few white precipitate drops of a solution of sulphate of copper as a trial with sulphate of test. The production of a whitish precipitate will indicate the presence of oxalic acid.
3. Production of oxalate of lead. Add to the filtered liquid acidulated with acetic acid a solution of acetate of lead ; if any oxalic acid be present, a precipitate will be produced either white or coloured by the organic liquid ; add more of the reagent until no further precipitation occurs.
4. Production of oxalic acid from the above precipitate. Collect the precipitate upon a filter, and wash it thoroughly, mix it up with water as to make a thin magma ; through this pass a current of sulphuretted hydrogen gas until the liquid, after having stood for a minute or so, smells strongly of the gas. Heat the whole for some time, allow the precipitate to subside, and filter. The filtrate will be an aqueous solution of oxalic acid, which, either with or without concentration, will yield all the above described reactions of oxalic acid in solution.
5. Production of oxalate of ammonia. This process may be adopted instead of the preceding :—Collect and wash the precipitate as from the same before, and then boil it for some time with a small quantity of diluted sulphuric acid—filter—neutralise with ammonia (should any precipitate occur, remove it by subsidence or filtration), and then apply the sulphate of lime and nitrate of silver tests for oxalic acid.

*Note.*—For certain objections to some of the above tests as being also applicable to alkaline oxalates, and vegetable decoctions containing them, consult "Taylor on Poisons," pages 260, 261, &c.

#### D.—IN THE INSOLUBLE FORM.

Combined with lime or magnesia, the result of the exhibition of one or other of these substances as antidotes.

Boil the insoluble white deposit for some time with an equal quantity of carbonate of soda in water, filter, neutralise the filtrate with dilute nitric acid, and apply the nitrate of silver and sulphate of lime tests for oxalic acid.

#### CORROSIVE SUBLIMATE.

##### A.—IN THE SOLID STATE.

1. Volatility. Heat a small portion of the powder on platinum foil ; it will volatilise entirely.
2. Solubility in water. To a little water in a test tube add a portion of the powdered salt, and heat gently, the powder will dissolve entirely.

3. Metallic reduction Mix a little of the powdered salt with about when heated with three times its bulk of calcined carbonate of soda, carbonate of soda. made warm and perfectly dry ; introduce a little of the mixture into a reduction tube also hot and dry, and apply heat, in the upper part of the tube a ring of metallic globules will be formed.
4. Detection of chlorine Cut off the bottom of the tube containing the residue in the re-fused residue ; boil it in water ; add a few drops, residue from the first of nitric acid and then of a solution of nitrate above experi- of silver ; a white precipitate will be formed, insoluble in nitric acid but soluble in ammonia.

#### B.—AQUEOUS SOLUTION.

1. Formation of crystals on evaporation Place a few drops of the solution upon a glass plate ; apply heat very cautiously ; as soon as a solid film appears at the margin of the liquid set it aside to crystallize ; on cooling, slender opaque intersecting needles will be formed which will afford the above described reactions of the solid poison.
2. Yellow precipitate To a portion of the solution in a test tube add with lime or an excess of lime or potash water ; an orange-potash water. yellow precipitate will be produced ; filter and test in the filtrate for chlorine, by means of nitrate of silver.
3. Scarlet precipitate To a portion of the solution in a test tube add with iodide of a drop or so of iodide of potassium solution ; an orange or scarlet precipitate will be produced ; add more of the reagent and the precipitate will be dissolved.
4. Production of black sulphuret of mercury. To the solution of the salt add an excess of sulphuretted hydrogen water, or a solution of sulphide of ammonium ; a dense black precipitate will be produced insoluble in nitric acid.

*Note.*—The reactions with potash, iodide of potassium, and sulphide of ammonium, may be easily obtained by adding a few drops of the respective agents to the powdered poison, or to the crystals left by the evaporation of the solution.

5. Metallic reduction To a portion of the solution add a few drops of by means of a hydrochloric acid, and then a solution of proto-proto salt of tin. chloride of tin ; a white precipitate (calomel) will be at first produced ; add more of the reagent, and the precipitate will become gradually slate coloured, and finally black ; heat gently ; allow the deposit to subside ; pour off the supernatant liquor, and boil the residue with hydrochloric acid ; globules of metallic mercury will be produced.

6. Precipitation by metals. Acidulate the solution with hydrochloric acid, and introduce into the fluid a piece of clean copper foil or gauze, which will speedily receive a silver like coating of mercury ; dry the slip of foil or gauze, put it into a dry reduction tube, and heat ; globules of metallic mercury will be found in the upper part of the tube.

7. Galvanic test. Coil a small piece of zinc foil around a similar piece of clean copper foil or gauze ; suspend the coil in the solution by means of a thread ; mercury will be deposited on both metals, most visibly of course on the copper ; dry the coil ; place it in a reduction tube, and apply heat ; mercurial globules will be condensed in the upper part of the tube. Or put a few drops of the solution upon a sovereign, then touch both the gold and the fluid with a piece of steel or zinc, a silver stain will be produced which will disappear on heating the coin.

#### C.—IN ORGANIC LIQUIDS.

In liquids containing organic matter, the re-action with a protosalt of tin may occasionally be employed, but the galvanic test, and the test of metallic reduction upon copper, are most applicable ; acidulate the liquid with muriatic acid, heat gently, and apply the tests as before.

*Note.*—In liquids containing organic matter it is sufficient to prove the presence of mercury, without taking the chlorine into consideration.

#### D.—MERCURY IN ORGANIC SOLIDS.

It will generally be sufficient to boil the broken up solid in water acidulated with hydrochloric acid, and then to apply the galvanic or metallic reduction upon copper tests as above. Occasionally, however, as in the detection of absorbed mercury in the tissues, it will be necessary to treat the broken up solid with concentrated nitro muriatic-acid, to evaporate to dryness in a water bath, to dissolve the residue in a small quantity of warm water, and then to apply the tests.

### LEAD.

#### A.—SOLID COMPOUNDS OF LEAD.

Metallic reduction. Lead may be readily procured in the metallic state from substances containing it in moderate quantity. Mix a small portion of a lead compound with three or four times its bulk of black flux ; heat the mixture on charcoal in the reducing flame of the blowpipe ; a malleable metallic globule will be produced, and the charcoal will receive a yellow incrustation. The globule may be dissolved in nitric acid, and to the solution thus formed the liquid tests can be applied.

## B.—IN SOLUTION.

1. Black precipitate, Hydro-sulphuric acid gas or its solution in water, with sulphuret- when added to any solution containing lead, whe-  
ted hydrogen. ther acid, alkaline, or neutral, gives a black or dark brown precipitate, (occasionally reddish col-  
oured) insoluble in cold muriatic acid.
2. White precipitate, Add to the solution of the poison some diluted sulphuric acid ; a white precipitate will be pro-  
duced insoluble in nitric acid, soluble in hydro-  
chloric acid, and soluble in a considerable excess  
of potash water ; the precipitate itself will be  
turned of a black colour by sulphuretted hydrogen.
3. Yellow precipi- Add to the lead solution, which must be made  
tate, with iodide nearly neutral, iodide of potassium ; a bright yellow  
of potassium. precipitate will be produced, soluble in hydro-  
chloric acid and in potash water.

*Note.*—The re-actions numbered 1 and 3 may be readily obtained by adding to the solid lead salt in a saucer, a few drops of the respective re-agents.

## C.—IN ORGANIC LIQUIDS.

1. Precipitation as Filter or strain the liquid if necessary ; acidulate sulphuret, and it with a few drops of nitric acid, and pass through subsequent solu- it a current of hydro-sulphuric acid, until it retains tion.  
for some time the smell of the gas ; a dark brown or black precipitate will be produced ; allow this to subside, then collect it on a filter and wash ; boil the washed precipitate in a mixture of one part of nitric acid with four parts of water, until the black colour is destroyed ; filter if necessary, and to the clear solution apply the tests for aqueous solutions of lead salts.

## D.—IN ORGANIC SOLIDS.

1. Incineration, and Dry the organic substance ; incinerate it in an subsequent solu- earthen or porcelain crucible ; boil the ash in tion.  
nitric acid, dilute and filter ; to the filtrate apply the tests.

## E.—CARBONATE OF LEAD.

1. Metallic reduction. *Vide supra.*
2. Colour, solubility, &c. Carbonate of lead occurs as a white powder which is turned yellow by heat, turned black by sulphide of ammonium, is insoluble in water, soluble in dilute nitric acid with effervescence ; certain impurities generally remain undissolved ; to the solution thus found the liquid tests can be applied.

## F.—ACETATE OF LEAD.

- Metallic reduction. *Vide supra.* In this instance carbonate of soda will answer as well as black flux.

2. Physical properties. Acetate of lead generally occurs as a crystalline powder of a white colour, a peculiar sour smell, and a sweetish taste; it is soluble in distilled water, and forms a milky liquor with common water; the solution when evaporated upon a glass plate yields opaque white prismatic crystals.

3. Chemical characters. Heat a portion of the original powder, or of the crystals procured by evaporation, in a test tube with a little dilute sulphuric acid; the smell of acetic acid will be given off; if the salt be treated with strong sulphuric acid and a little spirit of wine, the smell will be that of acetic ether. The crystals and powder are turned of a black colour by sulphide of ammonium, and of a yellow colour by iodide of potassium. When the salt is heated in a reduction tube it melts, resolidifies, becomes dark in colour, gives out a smell of acetic acid, and leaves behind a carbonaceous mass containing very minutely divided metallic lead.

## COPPER.

### A.—IN SOLUTION.

1. Colour. Such of the salts of copper as are insoluble in water are readily soluble in dilute mineral acids. The solutions, whether aqueous or acidulous, have a decidedly blue or green colour.

2. Production of sulphide of copper. To the cupreous solution, add hydrosulphuric acid, or sulphide of ammonium; according to circumstances, a chocolate-brown or brown-black coloured precipitate will be produced—divide the turbid liquid into three portions: to one, add excess of sulphide of ammonium, the precipitate will not disappear; to another, add hydrochloric acid, no solution will take place; to the third, add nitric acid, the precipitate will dissolve.

3. Deep blue solution with ammonia. Add carefully to the cupreous solution a few drops of ammonia, a bluish white precipitate will be produced; add more of the reagent, the precipitate will dissolve, and a deep blue-coloured liquid be formed. This liquid may be distinguished from the similarly coloured ammoniacal solution of nickel by the addition of caustic potash, which does not disturb the transparency of the cupreous, but affords a pale-green precipitate with the nickel solution.

4. Chocolate red-coloured precipitate ferrocyanide of potassium, a gelatinous chocolate with ferrocyanide will be produced. This anide of potassium precipitate is perfectly soluble in a mixture of potash and ammonia, forming a deep blue solution, in which respect it differs from the similarly coloured ferrocyanide of uranium. Ferrocyanide of potassium will precipitate an ammoniacal solution of copper after dilution with water, provided the ammonia be not in very great excess.

5. Metallic precipitation upon iron. If a piece of polished iron (needle or clean wire) be immersed in an acidulated cupreous solution, in the course of a minute or two metallic copper, having its characteristic colour, will be deposited thereon. If the amount of copper in the solution is very minute, the iron should continue immersed for an hour or more. Occasionally the deposit is not sufficient in quantity to present the ordinary aspect of metallic copper, but appears simply brown or black.

6. Examination of the metallic deposit by ammonia and ferrocyanide of potassium. Put the coated iron into a small capsule, and add to it a little ammonia. By exposure to the air the copper will dissolve in the ammonia, forming the above-described deep blue solution; allow the excess of ammonia to evaporate, and then add a drop or two of ferrocyanide of potassium, the chocolate red ferrocyanide of copper will be produced.

7. Galvanic precipitation on platinum. Put a drop or two of the acidulated cupreous solution upon platinum foil, or into a small platinum capsule, touch the platinum through the solution with a strip of zinc, metallic copper will be deposited upon the platinum either with its usual characteristic appearance, or simply as a brown stain. The deposit can be tested with ammonia and ferrocyanide of potassium, as in reaction No. 6.

#### B.—IN ORGANIC LIQUIDS.

1. Colour. Organic liquids containing copper are more or less of a greenish colour.

2. Metallic precipitation upon iron or platinum. Acidulate the liquid with hydrochloric acid, and apply the tests 5, 6, and 7, as previously.

3. Precipitate with hydrosulphuric acid. In order to remove the copper from an organic liquid, acidulate it with hydrochloric acid, filter, and pass through the filtrate a current of sulphuretted hydrogen gas. A brown-black precipitate will be produced, which may be collected

upon a filter, washed with water, dissolved in dilute nitric acid, and the solution tested as before.

### C.—IN ORGANIC SOLIDS.

1. Action of ammonia.      Organic solids, when containing even very small quantities of copper, become of a deep blue colour when immersed in ammonia.
2. Action of nitric acid.      In order to dissolve the copper out of an organic solid, cut it up into small pieces, and boil for some time in a mixture of one part of nitric acid with about five of water, filter, evaporate off the excess of acid, and apply the tests 5, 6, and 7, as before.

## ARSENIC.

### A.—SOLID ARSENIOUS ACID.

1. Appearance.      Arsenious acid, or white arsenic, occurs as a heavy white powder, or in transparent vitreous masses, or in opaque porcellanous masses, or in masses which are opaque externally, and glassy in the centre.
2. Volatility.      Heat a minute quantity of the powder on platinum foil, it will volatilise with the evolution of opaque white fumes : any fixed residue is an impurity, probably sulphate of lime. Put a little of the powder into a reduction tube, and apply heat ; a crystalline sublimate will form in the cold part of the tube. The sublimate has an iridescent appearance, and when examined by a lens is seen to consist of octa- and tetrahedral crystals.
3. Garlic odour.      Sprinkle a minute quantity of the powder upon red-hot charcoal, scarcely visible vapours, having a peculiar garlic odour, will be given off.
4. Action of sulphide of ammonium.      To a little of the powder in a watch glass add a few drops of the sulphide of ammonium, no alteration in colour will be perceived ; heat gently, the powder will be dissolved, and on evaporation an orange-yellow film will remain, soluble in alkalies, insoluble in hot hydrochloric acid.
5. Immiscibility with water.      Put some water into a test-tube, then add a little of the powdered arsenious acid, and agitate them together, the powder will not dissolve, but will remain partly as a film upon the surface, and partly in small lumps at the bottom. This condition will not disappear, even upon boiling ; by filtration, however, a clear aqueous solution of

arsenious acid will be produced. If the mixture of arsenious acid and water be heated, either with potash or with hydrochloric acid, complete solution will occur.

#### 6. Reduction test.

Mix a little of the powder with three or four times its bulk of dry soda flux, introduce a little of the mixture into a reduction-tube made perfectly dry and warm, and apply heat gradually; a steel grey-coloured ring of reduced metal will condense in the upper or cool part of the tube. When dealing with very minute quantities proceed as follows: drop the arsenic into a dry reduction-tube, then add three or four times its bulk of well-dried charcoal-powder, and apply heat cautiously, so that the upper layer of the charcoal shall be at a high temperature before the arsenic begins to volatilise; the ring of reduced metal will appear as before.

#### 7. Characters of the metallic ring.

The arsenical ring is recognised as follows:

1. By its brilliant steel-grey colour. Should the ring have an opaque brownish-black colour, apply heat very cautiously, when the metallic grey ring will remain, and a more volatile compound of arsenic be volatilised. The interior surface of the sublimate, rendered visible by breaking the tube, has a crystalline appearance.
2. By its volatility. By heating the sublimate carefully, it may be volatilised from one part of the tube to another.
3. By its conversion into arsenious acid. After repeated volatilisations up and down the tube, the ring of metal is gradually replaced by a ring of crystals of arsenious acid, or the piece of tubing containing the sublimate may be filed off, crushed, transferred to another reduction-tube, and heat again applied, when a sublimate will be produced which may be seen by a lens to consist of octa- and tetra-hedral crystals. These may be boiled in water for some time, when a solution will be found, to which the liquid tests can be applied; or they may be treated with nitric acid, to which a few drops of hydrochloric acid have been added, evaporated carefully to absolute dryness, then dissolved in a drop or two of water, and tested with the ammonio-nitrate of silver, which will give rise to a brick-dust red precipitate of arseniate of silver: soluble in ammonia.

#### B.—IN AQUEOUS SOLUTION.

##### 1. Reaction, &c.

The aqueous solution of arsenious acid is clear, colourless, tasteless, inodorous, and has a faintly acid reaction on test-paper.

2. Formation of crystals upon evaporation. Evaporate a little of the solution upon a glass plate, a white residue will be left, which, when examined by a lens, will be seen to consist of minute octo- and tetra-hedral crystals. These may be volatilised by a further application of heat.

3. Yellow precipitate with ammonio-nitrate of silver. To a strong solution of nitrate of silver, add a dilute solution of ammonia, drop by drop, until the brown precipitate at first produced is just redissolved. Add a few drops of the reagent thus prepared to the solution of arsenious acid, an opaque yellow precipitate will be produced, soluble in ammonia, soluble in nitric acid.

4. Yellow precipitate with ammonio-sulphate of copper. To a dilute solution of sulphate of copper add ammonia carefully, drop by drop, until the precipitate at first produced is nearly redissolved; add this reagent in small quantities to the solution of arsenious acid, a green precipitate will be produced, soluble in ammonia and in all acids. If the precipitate be collected on a filter, washed, dried, and heated in a reduction-tube, crystals of arsenious acid will sublime.

5. Yellow precipitate with hydrosulphuric acid. Through a solution of arsenious acid, acidulated with acetic or hydrochloric acid, pass a current of washed sulphuretted hydrogen gas, in excess—an abundant golden-yellow coloured precipitate will be produced. Sulphide of ammonium does not give any precipitate in aqueous solutions of arsenious acid until after the addition of a mineral acid.

6. Characters of the above precipitate. Collect the precipitate upon filtering paper, wash it with water, and test it as follows:—Boil a portion of it with hydrochloric acid—it will not dissolve; boil another portion with nitric acid—the precipitate will disappear with the formation of red fumes, a globule of melted sulphur probably remaining undissolved. To three other portions of the precipitate add respectively ammonia, carbonate of ammonia, and sulphide of ammonium—in each instance the precipitate will be redissolved, and in each instance be redeposited on the addition of hydrochloric acid. Dry the remainder of the precipitate, heat a portion of it in a reduction-tube—it will sublime unchanged; mix another portion with about four times its bulk of soda flux, put the mixture into a reduction-tube, and apply heat—a ring of reduced metal will condense in the upper part of the tube.

## C.—MARSH'S TEST.

If a substance containing arsenic be added to a mixture of metallic

zinc, with dilute sulphuric or hydrochloric acid, a gaseous compound of arsenic and hydrogen, known by the name of arseniuretted hydrogen, will be given off. Any of the ordinary forms of hydrogen apparatus may be employed—even the adaptation to one another of an apothecary's vial, a perforated cork, and a piece of glass tubing drawn out to a moderately fine point, will answer the purpose. The most convenient instrument, however, consists of the original bent tube designed by Marsh, with the addition of two bulbs, one in each limb.

In order to make use of this instrument proceed as follows:—Remove the stop-cock from the apparatus, and put into the shorter limb a piece of glass rod. This must be sufficiently small to fall to the bend of the tube, and not small enough to pass into the longer limb; a glass stopper will often answer the purpose extremely well. Now let fall upon the piece of glass a moderately small, compact mass of metallic zinc, replace the stop-cock, and pour into the longer limb diluted sulphuric acid, in the proportion of about one part of acid to seven or eight of water, so that when the liquid is level in the two limbs there may still remain some little free space beneath the stop-cock. Allow the acid to act upon the zinc for a few minutes, and then close the stop-cock: the shorter limb will become gradually filled with hydrogen gas, the acid being necessarily driven up into the longer limb. Open the stop-cock, and quickly set fire to the hydrogen—it will burn with a scarcely visible flame; momentarily depress upon the flame a piece of clean glass or porcelain, there should be no deposit, nor even a discolouration, produced thereon. As soon as the acid has replaced the hydrogen, close the stop-cock. Repeat the above experiment several times, so as to be perfectly assured of the purity of the hydrogen.

1. Appearance of the flame. Pour into the longer limb the arsenical liquid, allow the hydrogen to escape for a minute or so, close the stop-cock, collect the gas, and set fire to it as before—it will burn with a peculiar bluish-white flame, and evolve an opaque white smoke.
2. Nature of the smoke. The white smoke consists of arsenious acid; it is best tested as follows. Hold over the summit of the flame a piece of porcelain, that has been moistened with ammonio-nitrate of silver—a yellow deposit of arsenite of silver will be produced. Or, hold over the flame, more than once if necessary, a short and wide test tube, moistened on its interior with water,—then add a little more water, and test the liquid with hydrosulphuric acid or ammonia-nitrate of silver.
3. Formation of a deposit. Momentarily depress upon the flame, so as to cut off about one half of its height, a piece of clean glass or porcelain,—a dark stain or deposit will be produced thereon: this deposit is constituted of three products,—in the centre of metallic arsenic

in the exterior of arsenious acid, and in the intermediate portion, of a compound generally considered to be a suboxide of arsenic.

That the stain is really arsenical is shown by its possessing the following properties—

- a.* Metallic brilliancy. The lustrous appearance of the arsenical stain is best seen on its free surface ; it is, however, recognisable through the glass.
- b.* Hair brown colour. This character belongs particularly to the intermediate portion of the deposit, and is best seen by transmitted light.
- y.* Volatility. The arsenical stain volatilizes very readily on the application of heat. This quality is very manifest when the stain has been produced upon a thin plate of talc ; the metallic arsenic during the volatilization becomes converted into arsenious acid.
- d.* Conversion into arsenic acid. Collect the deposit in a watch-glass, add a couple of drops of hydrochloric and one of nitric acid, evaporate cautiously to dryness, add one or two drops of water, there will be no turbidity produced ; then add a drop of the ammonio-nitrate of silver, a brick dust red precipitate will be formed.
- e.* Solubility in chloride of lime. Add a few drops of a solution of chloride of lime (bleaching powder), to the deposit on a watch-glass ; complete solution will speedily take place.

*Note.*—Compare the above characters with those described under the head of Antimony, page 62.

By proceeding as follows these two modifications of Marsh's process may be performed together.

1. Action on nitrate of silver. Allow the hydrogen to be developed from an ordinary gas generating bottle. Let the cork be perforated by a narrow piece of hard German tubing, bent twice at right angles so as to have a short vertical limb attached to the cork, then a tolerably long horizontal portion, then a second vertical limb, reaching to within an inch of the level of the bottom of the bottle, and dipping into a vessel containing a solution of nitrate of silver. Test the purity of the hydrogen, and as soon as its evolution becomes moderate and regular add the arsenical liquid : as the arseniuretted gas bubbles through the silver solution, a deposition of black flocculi will take place. Apply the heat of a spirit or gas lamp to the horizontal portion of the tube ; a ring of metallic arsenic will be deposited some little distance in front of the flame.
2. Decomposition by passing through a red hot tube.

The ring of metal may be shown to be arsenic by its volatility, and by its conversion into crystal-

line arsenious acid, which may be examined by the usual tests. To the silver liquid add a sufficiency of hydrochloric acid to throw down the whole of the silver, filter, evaporate the filtrate to dryness, dissolve the residue in water, and add the ammonio-nitrate of silver, when a brick dust red precipitate will be produced.

#### D.—REINSCH'S TEST.

This test is particularly useful for the detection of arsenic in organic liquids or solids. The suspected liquid is simply to be acidulated with about one-sixth of its bulk of hydrochloric acid and boiled. The solid tissue must be cut up into very small pieces, and boiled for some time in a mixture of about one part of hydrochloric acid with six of water, until the whole is completely disintegrated, then strained through muslin, or filtered through a previously wetted filtering paper.

1. Deposit on copper. Into either of the above boiling liquids, dip the end of a piece of clean polished wire, examine the wire from time to time, and as soon as its surface acquires a grey metallic discolouration remove it, and add in its stead fragments of fine copper gauze, continuing the supply as long as the last added piece assumes any definite alteration in colour.
2. Production of arsenious acid. Remove the pieces of copper gauze, wash them in water, and dry them between folds of filtering paper; the deposit will not rub off unless the amount of arsenic be very large. If the arsenic exists in but very small quantity, the colour of the precipitated metal is bluish, otherwise of a dark iron grey tint. Holding the piece of gauze in the fingers warm it over a flame, coil it up into a small compass, and introduce it into a reduction tube; now apply heat cautiously, the arsenic will volatilise, oxidise, and condense in the cold part, in the form of a white crystalline sublimate: several pieces of coated gauze may be thus treated successively, until a sufficiently obvious sublimate of arsenious acid is procured; by examination with a lens, or with the low power of a microscope, the crystals will be seen to consist of highly iridescent octo- and tetra-hedra.
3. Production of red arseniate of silver. File off the piece of tube containing the sublimate, fold it in glazed paper, and crush it; drop from the above the fragments into a short, wide test tube, add four or five drops of hydrochloric, with two or three of nitric acid, and evaporate the whole carefully to perfect dryness; then add a drop or two of the ammonio-nitrate of silver, when a brick dust red precipitate will be produced.

## E.—IN ORGANIC MIXTURES.

Destruction of organic matter. Reinsch's process, above described, is by far the most applicable: however, Marsh's test, or the sulphuretted hydrogen test, may be employed.

1. Marsh's process. The great inconvenience in the use of Marsh's test arises from the frothing of the liquid: to avoid this, evaporate the organic matter to dryness, and heat the residue with a small quantity of concentrated sulphuric acid just sufficient to moisten the whole: as soon as the charred mass is dry and friable, boil it in water, and pour the clear solution into Marsh's apparatus. For the sulphuretted hydrogen test the organic solution may be prepared as for Reinsch's process, and the hydro-sulphuric acid passed through the cold liquid; the resulting yellow precipitate is then to be treated with ammonia, and the ammoniacal filtrate evaporated to dryness: if the dry residue be then mixed with four or five times its bulk of soda flux, and heated in a reduction tube, a ring of metal will condense in the cold part of the tube.
2. Hydrosulphuric acid test.

## F.—OTHER FORMS OF ARSENIC.

The sulphurets of arsenic (orpiment and realgar), are yellow or orange coloured substances; when heated in reduction tubes they volatilize unchanged. When mixed with soda flux and heated in reduction tubes, they give rise to metallic sublimes, and the residues, when moistened with hydrochloric acid, evolve sulphuretted hydrogen, which is known by its smell and by its action on lead paper. These sulphurets are not perceptibly dissolved by boiling hydrochloric acid, but the acid liquor can be successfully examined for arsenic by Reinsch's and Marsh's tests.

Arsenite of copper is a green-coloured powder: when heated in a reduction tube, it yields a crystalline sublimate of arsenious acid, which may be further examined; and a black residue of oxide of copper, which may be dissolved in hydrochloric acid, and examined for copper by the usual tests. Arsenite of copper is soluble in hydrochloric acid, and the solution may be tested by Reinsch's and Marsh's processes.

## ANTIMONY.

## A.—IN SOLUTION.

1. Orange precipitate with hydrosulphuric acid. Acidulate the solution with tartaric acid, and pass through it a current of hydrosulphuric acid, until the smell of the gas remains permanently—an orange yellow precipitate will be produced; throw the whole on to a filter, wash the precipitate well with water, and test it as follows. Heat a portion of it with a solution of sesquicarbonate of ammonia,

it will not dissolve. Heat another portion with sulphide of ammonium, complete solution will take place, but on the addition of an acid the orange sulphide will be reprecipitated. Heat another portion of the precipitate with strong hydrochloric acid it will be entirely dissolved ; boil off any excess of acid and pour the remainder into a glassfull of water, an abundant white precipitate will be produced.

## 2. Reinsch's test.

This is sometimes useful as a trial test : proceed as in testing for arsenic : the antimonial deposit on the copper has more of a violet colour than has the arsenical : if the copper gauze be dried and heated in a reduction tube, the antimony if in small quantity will volatilise, oxidise, and give rise to a slight whitish amorphous sublimate.

## B.—MARSH'S TEST.

This test is particularly applicable for the detection of minute quantities of antimony. If the sulphuretted hydrogen test has afforded good results, this process is quite unnecessary. If the antimonial solution be poured into a charged Marsh's apparatus, antimoniumuretted hydrogen will be given off and may be ignited ; it will burn with a flame somewhat similar to that of arsenic ; it will likewise give off a white smoke, which, however, will not produce any effect upon the ammonio-nitrate of silver.

### 1. Formation of a deposit on glass or porcelain.

Ignite the gas and depress upon the flame a piece of glass or porcelain, a dark stain or deposit will be produced, which may be distinguished from the arsenical stain by the following characters :  $\alpha$ . by its want of metallic lustre,  $\beta$ . by its smoky black colour,  $\gamma$ . by its comparative want of volatility,  $\delta$ . if it be treated with nitro-hydrochloric acid and evaporated to dryness, the residue obtained will not yield a red precipitate with the ammonia-nitrate of silver,  $\epsilon$ . it is insoluble in a solution of chloride of lime.

## C.—IN ORGANIC MIXTURES.

The sulphuretted hydrogen and Reinsch's process are perfectly applicable to organic liquids : should there be any sediment to the liquid, the whole should be digested for some time with a solution of tartaric acid, and then filtered. Organic solids must be thoroughly dried, heated with nitro-muriatic acid, boiled and filtered.

## D.—TARTAR EMETIC.

Tartar emetic occurs as a white powder or in white ill-defined crystalline masses ; it affords the above described reactions of antimony : it

becomes charred by heat, and is turned of an orange colour by the addition of sulphide of ammonium ; it is soluble in water, which solution by careful evaporation yields tetrahedral crystals ; the addition of nitric or other mineral acid to the solution gives rise to a white precipitate.

#### E.—CHLORIDE OF ANTIMONY

Is a highly corrosive fuming liquid, generally having a yellow or orange colour from the presence of chloride of iron ; it affords the above described reactions of antimony ; if poured into water it gives rise to an abundant white precipitate ; this when collected in a filter and well washed, becomes of an orange colour on the addition of sulphide of ammonia, and is soluble in tartaric acid.

#### OPIUM.

##### A.—MORPHIA.

The salts of morphia are soluble in water ; morphia itself is very slightly soluble in pure water, but readily soluble in acidulated water. The following tests may be applied to morphia, or its salts in the solid state, or to moderately concentrated solutions.

1. Action of potash. To a concentrated solution of a morphia salt add one drop only of caustic potash, and stir, a white precipitate will be produced ; add more of the reagent, the precipitate will disappear.
2. Deep orange colour with nitric acid. To a cold solution of a morphia salt, add about an equal bulk of strong nitric acid, a deep orange red colour will be gradually developed—or place a little powdered morphia in a watch glass and add to it a few drops of the strong acid, the above described orange red colour will be instantaneously produced : other alkaloids react in a similar way with this test.
3. Green colour, with sulphuric acid and bichromate of potash. To a morphia solution in a test tube, add an equal bulk of strong sulphuric acid and agitate well ; then pour in carefully a solution of bichromate of potassa, a deep green colour will be developed at the junction of the two liquids,—or to a little powdered morphia in a watch glass, add a few drops of strong sulphuric acid, mix the two substances with a glass rod, and then sprinkle them with some finely powdered bichromate of potash, a deep green colour will be produced. If instead of bichromate of potash nitrate of potash be employed, a greenish brown colour is produced. Narcotina, which acts similarly to morphia upon the bichromate, is turned of a beautiful crimson colour by the mixture of sulphuric acid and the nitrate.
4. Blue colour, with a persalt of iron. To a solution of morphia, or to the dry powder, add a drop or two of a neutralised solution of perchloride of iron, a blue or greenish blue colour will be developed.

5. Decomposition of morphia. To a solution of morphia, add a minute quantity of iodic acid; for of diluted starch paste, and then a few drops of mation of blue iodic acid, the blue iodide of starch will be iodide of starch. speedily produced; or place a little of the powder upon a piece of starch paper, and moisten it with a little iodic acid, the paper will be stained of a purplish blue colour.

#### B.—OPIATE LIQUIDS.

Our object in the examination of liquids containing opium is to detect the morphia and the meconic acid. This last body, though not poisonous, is characteristic of opium, and is possessed of well-marked properties.

1. Nitric acid as a trial test for morphia. If the opiate liquor be not very dark coloured, add to it a considerable quantity of strong nitric acid, the development of an orange red colour will indicate the probable presence of morphia. In order to lessen the original colour of the opiate liquid, it may if necessary be slightly diluted with water.
2. Perchloride of iron as a trial test for meconic acid. If the opiate liquid be dark-coloured, dilute it with a very considerable quantity of water, so as to produce a moderately pale solution, and then add a little perchloride of iron. If meconic acid be present even in small quantity, a distinct reddening of the liquid will be produced.
3. Formation of meconate of lead and acetate of morphia. Acidulate the opiate liquid with acetic acid, and then add a solution of acetate of lead as long as it continues to produce a precipitate, agitate the whole, and filter. Meconate of lead will remain as an insoluble substance upon the filtering paper, while the filtrate will contain acetate of morphia together with the excess of acetate of lead.
4. Production of meconic acid from the meconate of sulphuric acid and filter: the filtrate will be a solution of meconic acid.
5. Testing the meconic acid with a persalt of iron. To the above filtrate add a little perchloride of iron: a well-marked dark logwood red colour will be produced, owing to the formation of meconate of iron. The liquid will not alter its colour on boiling, in which respect it differs from the similarly coloured solution of acetate of iron, neither will it be bleached on the addition of corrosive sublimate, in which respect it differs from the similarly coloured solution of sulphocyanide of iron.
6. Purification of the acetate of morphia. Through the liquid filtered from the precipitate of meconate of lead, pass a current of sulphuretted hydrogen, until the liquid smells persistently

of the gas, filter, concentrate the filtrate by evaporation, boil with a little animal charcoal, refilter, and to the clear filtrate apply the above described tests for morphia, particularly that with nitric acid and that with iodic acid.

NOTE.—The above-detailed processes for the separation of meconic acid and morphia are equally applicable to other organic liquids, such as the contents of the stomach. Organic solids, such as the tissue of the stomach, must be digested for some time in dilute acetic acid, before precipitation with the acetate of lead is resorted to.

## PRUSSIC ACID.

### A.—REACTIONS IN THE LIQUID STATE.

1. Physical characters. Prussic or hydrocyanic acid is a colourless, perfectly volatile, faintly acid, mobile liquid. Its vapour, which is given off at all ordinary temperatures, is invisible, has an odour said to be like that of oil of bitter almonds, and when inspired even in minute quantities causes a peculiar sensation in the fauces.
2. White precipitate To a little of the acid in a test tube add a few drops of solution of nitrate of silver, a white clotty precipitate will be produced ; agitate the whole briskly, allow the precipitate to subside, and pour off the supernatant liquid as completely as possible. Introduce a little of the precipitate into a test tube, and add three or four times its bulk of concentrated nitric acid ; it will remain unacted upon ; boil for some time it will disappear more or less completely. Put a little of the precipitate into a watch glass and add a few drops of hydrochloric acid, the vapour of prussic acid will be given off, and may be received on to another watch glass, moistened with yellow sulphide of ammonium, or with a mixture of potash and sulphate of iron, as described under the head of the reactions of the vapour. Collect the remainder of the precipitate upon a filter, wash and dry it, put it into a reduction tube and apply heat : cyanogen gas will be given off, which may be ignited at the mouth of the tube, where it will burn with its peculiar rose-coloured flame : pulverulent metallic silver will remain in the reduction tube. The above described precipitate of cyanide of silver is moreover soluble in ammonia ; and also in potash, when the hydrocyanic acid remains in excess ; but these are comparatively unimportant characters.

3. Iron test. Formation of Prussian blue. For To a portion of the liquid acid, in a test tube, add a little potash water, and then a few drops of a solution of ordinary green vitriol that has been exposed to the air for a short time. A dingy greenish precipitate will be produced. Add hydrochloric acid, and the precipitate will become of a bright blue colour.

4. Sulphur test. To a little of the liquid acid in a capsule, add one or two drops of yellow sulphide of ammonium, and evaporate carefully to dryness, at as low a temperature as possible. Moisten the residue with water, and then add a drop or two of the solution of perchloride of iron; a blood-coloured liquid will be produced.

#### B.—REACTIONS OF THE VAPOUR.

The succeeding tests may be applied to the vapour of the pure liquid acid, to the vapour developed by the action of hydrochloric acid upon the precipitated cyanide of silver, or the vapour evolved from organic liquids or solids containing prussic acid.

1. Silver test. Moisten the interior of a watch-glass with a solution of nitrate of silver, and invert it over a second watch-glass, or other suitable vessel, containing the suspected fluid. An opaque white film will be produced in the silver solution; this is useful as a trial test.

2. Iron test. Formation of Prussian blue. Dissolve a few crystals of sulphate of iron in water; add a few drops of caustic potash, and expose the mixture for a short time to the action of the air. Smear the interior of a watch-glass with the dingy green compound thus produced, and invert it over a second watch-glass containing the suspected fluid, and resting on the palm of the hand, the warmth of which will serve to volatilise the acid. After a few minutes, or longer if the proportion of acid be very minute, remove the upper watch-glass, and add to it a drop or two of hydrochloric acid. A considerable proportion of the iron mixture will dissolve, and a bright blue coloured residue be left.

3. Sulphur test. Smear the interior of a watch-glass with the yellow solution of sulphide of ammonium; invert it over another watch-glass containing the suspected fluid, and resting upon the palm of the hand, as before. After a minute or two remove the upper watch-glass, and cautiously evaporate its contents to dryness, at as low a temperature as possible. Add to the residue a drop or two of perchloride of iron, when a blood-red colour will be developed.

# ANIMAL CHEMISTRY.

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## INTRODUCTION.

THE animal fluids and tissues consist of water together with a certain amount of solid matter. If an animal tissue or fluid be kept for some time at, or a little above, the temperature of boiling water, the aqueous portion evaporates off more or less completely, and the dry solids remain. If the dry residuum be heated upon platinum foil, it will undergo combustion ; some of its constituents will be dissipated, and a black carbonaceous mass remain. If this carbonaceous residue be further heated for some time, especially if in a current of air, the black colour will gradually disappear, and a white ash, fusible or infusible according to circumstances, will be left upon the foil. The components of a dried animal substance are thus separated into two classes ; the one comprising the substances which are destroyed by fire, and which are called the organic constituents ; the other comprising the substances which resist the action of fire, and which are called the inorganic constituents, or more simply the ashes. This distinction, however, is not absolute.

The organic components of animal matter consist principally of—

CARBON.

HYDROGEN.

OXYGEN.

NITROGEN.

SULPHUR and

PHOSPHORUS.

These are also called the elementary or ultimate principles of organic bodies.

The ashes consist principally of—

SODA.

POTASH.

LIME.

MAGNESIA.

OXIDE OF IRON.

SULPHURIC ACID.

PHOSPHORIC ACID.

CARBONIC ACID.

CHLORINE.

FLUORINE.

SILICA.

Nearly all animal products are composed of both organic and inorganic constituents : some few substances, however, belong almost entirely to one class : thus, while the enamel of the teeth contains scarcely any organic matter, some of the crystals of uric acid met with in the urine afford scarcely any ash.

In animal tissues or fluids, the ultimate organic principles are combined with one another in a variety of ways, constituting definite compounds, which are known as *proximate* organic principles : thus in urine we may have all the above-mentioned ultimate principles united with one another, so as to form the proximate principles,—urea, uric acid, sugar, albumen, &c.

The muscular tissue is a very suitable material to be employed for the demonstration of the principal organic and inorganic constituents of animal bodies : the same general plan is adopted in other instances.

## ULTIMATE ORGANIC CONSTITUENTS.

## 1.

**DESICCATION.**—Cut the flesh into small pieces and dry them in a water bath; a tough but yet pulverisable residue will be left. By this means the flesh has been separated into an aqueous portion which has evaporated, and a solid portion which remains. Nearly all animal matters behave in a similar manner, but nitrogenous substances having an alkaline reaction give off water containing a variable amount of ammonia.

## 2.

**DESTRUCTIVE DISTILLATION.**—Put a few fragments of the dried flesh into a reduction tube, and insert into the mouth of the tube a minute strip of rose\* (or red litmus) paper, and a similar strip of acetate of lead paper; on applying the heat of a lamp, water will condense in the upper part of the tube, proving the presence of *oxygen* and *hydrogen* in the flesh—a smell of ammonia will be given off, and the rose paper become green, results indicating the presence of *nitrogen*—the lead paper will become blackened, showing the presence of *sulphur*, and a black mass consisting chiefly of *carbon* will remain in the tube.

## 3.

**FUSION WITH NITRE.**—The following is perhaps a more generally applicable method of testing for sulphur and carbon. Mix a little of the powdered dried animal matter with an equal bulk of powdered nitre, and project the mixture in small portions at a time into a porcelain crucible kept at a red heat. Deflagration will ensue, and in the fused residue the presence of carbonic and of sulphuric acids may be readily manifested by the usual tests.

\* Paper saturated with a strong infusion of red rose petals forms a very delicate test for the presence of the alkalies, by the action of which the colour is changed from an almost imperceptible pink to a fine decided green hue. This paper was first brought into use by Dr. A. Taylor.

## 4.

**DETECTION OF SULPHUR.**—In bodies which are of a moderately light colour, sulphur may be tested for as follows. Put a little potash water into a test tube, and then add a drop of a solution of acetate of lead ; the white precipitate at first produced will speedily disappear on agitation. In this liquid boil the substance under examination : if it contains sulphur it will become stained of a brown or black colour, which colour cannot be removed by subsequent washing with water. If a substance is stained in the above manner when boiled in a potash solution of lead, and is scarcely or not at all deepened in colour when boiled in a simple solution of pure potash (free from lead), the presence of sulphur is certain. In the case of bodies readily soluble in potash water the results are not quite so characteristic.

It is questionable whether unoxidised phosphorus exists in any of the educts of the animal body, with the possible exception of certain phosphorised fats, which are found in the blood and in the nervous tissue : the phosphoric acid nearly always present in the ash of animal matters is believed to have existed as such in the original substance.

**Note.**—The student will do well to practise himself in the detection of these ultimate constituents of animal products : he will obtain very different results in experimenting with different substances,—such, for instance, as pieces of flannel, hard white of egg, refined gelatine, oxalate of lime, sugar, &c.

#### EXAMINATION OF THE ASH OF ANIMAL MATTER.

By the action of water, the ingredients of the ash may be divided into those which are soluble, and those which are insoluble. From this separation, however, we cannot infer anything with regard to the condition in which the salts

originally existed in the animal matter. Moreover, the process is in itself inconvenient, in consequence of the difficulty which frequently exists in filtering off the soluble from the insoluble portions. Where this difficulty does not exist, the separation by water may be employed. The separation effected by the following plan is almost identical with that produced by the action of water alone.

### 1.

**INCINERATION.**—Ignite some of the dried flesh upon a piece of platinum foil or in a small capsule : the flesh will swell up, burn with a smoky flame, and leave an abundant carbonaceous residue. Continue the application of heat for some time, the carbon will gradually burn away. Its disappearance will be facilitated by occasionally pulverising the coherent residue resulting from the ignition. Throughout the process the temperature should not exceed, or indeed scarcely arrive at, a full red heat. As soon as a white or pale grey ash is produced, the heating may be discontinued.

### 2.

**SOLUTION.**—Put some of the ash into a watch glass, moisten it with water, and add a few drops of nitric acid ; effervescence will indicate the presence of *carbonic acid*. Transfer the contents of the watch glass to a test tube, add more of the ash, also a little water, and if necessary nitric acid, boil and filter : any undissolved portion will consist almost entirely of carbon, and may be neglected.

### 3.

**PRECIPITATION OF PORTION INSOLUBLE IN WATER.**—Put a small piece of litmus paper into the above filtrate, and then add carefully, drop by drop, a dilute solution of ammonia, until the test paper just acquires an alkaline reaction ; then add a drop or two of a solution of carbonate of ammonia, agitate well and filter.

The precipitate may contain—	The filtrate may contain—
PEROXIDE OF IRON.	SULPHURIC ACID.
PHOSPHORIC ACID.	HYDROCHLORIC ACID.
LIME and	PHOSPHORIC ACID.
MAGNESIA.	POTASH and SODA.

## 4.

**EXAMINATION OF THE PRECIPITATE.**—Wash the precipitate with water, and dissolve it in the smallest sufficient quantity of hot dilute hydrochloric acid. To a portion of the liquid add a few drops of ferrocyanide of potassium ; the production of a blue colour will be indicative of *iron*. To another portion of the liquid add nitrate of silver, filter, and neutralise carefully with ammonia ; the production of yellow precipitate will be indicative of *phosphoric acid*. To the remainder of the liquid add acetate of ammonia ; a white or reddish brown precipitate of *phosphate of iron* may be produced, in which case boil and filter : to the filtrate add oxalate of ammonia in excess, a white precipitate will be formed indicative of *lime* : filter again, to the filtrate add ammonia, and if necessary stir for some time : the production of a white crystalline precipitate will be indicative of *magnesia*.

**Note.**—In the presence of a large amount of iron, not only will the above-described silver reaction of *phosphoric acid* be obscured, but it may even be necessary to add a little phosphate of ammonia in order to precipitate the *magnesia*. In any case the precipitate of *phosphate of iron* may be examined as follows : boil it for some time with caustic potash, and filter ; neutralise the filtrate with nitric acid, and test it for phosphoric acid by the silver or magnesia tests, wash the precipitate, dissolve it in dilute hydrochloric acid, and in the solution test for iron by any of the usual tests.

## 5.

**EXAMINATION OF THE FILTRATE.**—Divide the filtrate into two portions; acidulate one with nitric acid, and then add nitrate of baryta in excess ; the production of a white precipitate

will shew the presence of *sulphuric acid*. Filter, and to the filtrate add nitrate of silver; the production of white precipitate will show the presence of *hydrochloric acid*. Filter, and neutralise the filtrate carefully with a dilute solution of ammonia; the production of a yellow precipitate will indicate *phosphoric acid*. Evaporate the other portion of the solution to dryness, ignite the residue upon platinum foil, and dissolve it in a small quantity of water acidulated with hydrochloric acid; carefully evaporate a few drops of the solution upon a glass plate, or in a watch glass; cubical crystals of common salt will be formed, shewing the presence of *soda*. To the remainder of the solution add bichloride of platinum, and stir for some time if necessary; the production of a crystalline yellow precipitate will indicate the presence of *potash*. Where the separation of the alkaline from the earthy salts has been effected by water alone, one portion of the aqueous solution must be rendered slightly acid with hydrochloric acid, tested for soda by the formation of crystals of common salt, and after concentration tested for potash by the production of a yellow precipitate with bichloride of platinum; and the other portion tested for the acids as above.

Silica will be referred to when speaking of the urine; fluorine when speaking of bone.

### URINE.

Healthy human urine is an aqueous fluid, in which various substances, organic and inorganic, are dissolved, and certain other substances held in suspension. It has an amber colour, a slightly acid reaction, a characteristic though not powerful odour, and a specific gravity ranging within a few degrees of 1020.

The substances suspended in the urine are MUCUS and EPITHELIUM.

The dissolved organic constituents are UREA, URIC ACID, HIPPURIC ACID, COLOURING MATTER, and EXTRACTIVES.

The inorganic constituents are SODA, POTASH, MAGNESIA, LIME, PHOSPHORIC ACID, SULPHURIC ACID, and CHLORINE. The student will have to detect these different substances, and to verify their principal properties. For microscopic examination a good quarter-inch object-glass is required.

1.

MUCUS, EPITHELIUM, &c.—Pour some recent urine into a glass vessel, and set it aside for some little time; then, on holding the specimen between the eye and the light, a loose flocculent turbidity will be perceived in it. If this deposit be examined microscopically, it will be seen to consist of *epithelial scales* derived from different portions of the urinary apparatus, and of *mucus corpuscles*. By filtration, these undissolved urinary ingredients will remain as a scarcely visible deposit upon the filtering paper, and the urine itself pass through perfectly bright. By gently drying the filtering paper, the residue will assume a varnish-like aspect.

2.

DETECTION OF UREA.—Concentrate upon a glass slide a few drops of the filtered urine, and then add one or two drops of concentrated colourless nitric acid; a crystalline deposition of nitrate of urea will gradually take place. This deposit may be examined under the microscope, when it will be seen to consist of delicate six-sided plates, superimposed one upon the other, so that it will rarely happen that more than three or four of the sides of any one crystal will be visible. The nitrate of urea may be formed in a watch glass, and then examined on the slide, or it may be redissolved in water and the solution crystallised on the slide, or the nitric acid may be added to the concentrated urine previously placed in the field of the microscope, and the process of crystallisation observed.

3.

PREPARATION OF UREA.—Concentrate about a couple of ounces of filtered urine to a syrupy consistency, and then add finely-powdered oxalic acid in considerable excess,

or until the last added portions remain undissolved. On cooling the whole will become nearly solid, from the precipitation of oxalate of urea. Collect the semi-solid mass, and submit it to considerable pressure between several folds of coarse filtering-paper—a hard dry residue will be left. Transfer this dried cake, with the least possible amount of breaking, into a test-tube, and add rather more than an equal bulk of cold distilled water, agitate gently, and after some little time pour away the liquid, boil the residue in water, and filter the hot solution. Boil the filtrate with a little animal charcoal, and then add gradually some finely-powdered chalk as long as any effervescence is produced, filter, and evaporate the clear liquid in a water-bath. This liquid is an aqueous solution of urea, which when evaporated to a small bulk will deposit crystals. The crystallisation may be effected on a glass slide, and the result examined microscopically. Urea appears sometimes in the form of white silky needles, sometimes in the form of flattened four-sided prisms, containing numerous cavities.

## 4.

**PROPERTIES OF UREA.**—Urea is an organic base, capable of uniting with certain acids to form salts; it is soluble in water and alcohol; its solutions are neutral to test-paper; its formula is  $C^2N^2H^4O^2$ , or  $NH^4O$ ,  $C^2NO$  anomalous cyanate of ammonia. It can be prepared artificially. When boiled with caustic alkalies, it absorbs two equivalents of water, and splits up into two equivalents of carbonic acid, which unite with the fixed alkali and two equivalents of ammonia, which are set free,  $NH^4O + 2HO = 2NH^3 + 2CO^2$ . It behaves in a similar way when boiled with strong mineral acids, only that the ammonia unites with the acid, and the carbonic acid is set free. 1000 parts of urine contain on the average about 15 of urea.

## 5.

**DETECTION OF URIC ACID.**—This body occurs but in very small quantity in normal urine, 1000 parts of which

contain on the average about one-half part of the acid. To detect its presence, concentrate a couple of ounces of filtered urine to about half its bulk, add ten or a dozen drops of hydrochloric acid, and allow the whole to stand in a cool place for some hours, when the interior of the containing vessel will become studded with minute brownish crystals of impure uric acid. In the case of urine having a moderately high specific gravity, concentration is unnecessary. Having poured away the liquid, detach the crystals, wash them with water, dissolve them in a few drops of hot potash, filter, cool, and add hydrochloric acid in slight excess: a crystalline deposit will be produced, which may be examined microscopically and by the action of nitric acid, as described below.

### 6.

**PREPARATION OF URIC ACID.**—Uric acid cannot well be prepared in any quantity from normal human urine. It may, however, be readily obtained from uric calculi, or from the common brick-dust urinary deposit, or from the excreta of the boa. Pulverise the calculus or boa's excrement, or collect the lateritious deposit upon filtering-paper: boil any one of these substances with caustic potash, dilute with water, boil and filter, allow the filtrate to cool, and slightly supersaturate it with hydrochloric acid. On the addition of the acid a very considerable opacity will be at first produced, which, however, will speedily disappear, and be replaced by a dense crystalline precipitate, from which the supernatant liquid may be readily poured off.

### 7.

**PROPERTIES OF URIC ACID.**—Uric acid is a bibasic acid; its formula is  $C^{10}N^4H^2O^4$ ,  $2HO$ ; the formula for an acid urate,  $C^{10}N^4H^2O^4$ ,  $HO$ ,  $MO$ ; that for a neutral urate,  $C^{10}N^4H^2O^4$ ,  $2MO$ . The acid is extremely insoluble both in water and alcohol. It is soluble in alkaline solutions, from which it is reprecipitated on the addition of an acid. It always occurs in a crystalline condition; its appearance, however, being very variable. Occasionally it is met with in its normal form—

that of the rhombic prism, more generally in rhombic plates, with the obtuse angles more or less rounded off, or in acuminate doubly convex lozenge-shaped plates, or in elongated flat plates with excavated ends. The acid dissolves readily with effervescence in nitric acid, and if the solution be evaporated to dryness an amorphous pinkish residue remains. This, when moistened with ammonia, assumes a fine crimson colour, which is changed to violet on the addition of a minute quantity of caustic potash.

## 8.

**PREPARATION OF HIPPURIC ACID.**—This acid exists in very minute quantity in normal urine, so that it would be difficult for the student to obtain it therefrom. It can, however, be readily procured from the urine of the herbivora, or from the urine of patients who have been taking benzoic acid as a medicine. To prepare it from either of these sources proceed as follows:—Evaporate the recent filtered urine to about one-fourth of its bulk, and then add an equal quantity of strong hydrochloric acid: on cooling, long prismatic needles will crystallise out: collect the crystals, wash them with a little cold water, dissolve them in boiling water, filter the solution, and set it aside to crystallise. The crystals may if necessary be still further purified by re-solution, saturation of the hot liquid with chlorine gas, ebullition to remove the excess thereof, and subsequent crystallisation.

## 9.

**PROPERTIES OF HIPPURIC ACID.**—The formula for this acid is  $C^{18}NH^8O^5, HO$ . Hippuric acid is soluble in water and alcohol: if the alcoholic solution be evaporated upon a glass slide, the acid is deposited in plumose crystals, which are frequently arranged in a concentric form. The crystals procured by cooling the hot aqueous solution upon a slide consist of delicate four-sided prisms, which by an optical illusion often appear in the form of elongated six-sided plates. By prolonged boiling with concentrated hydrochloric acid, hippuric acid gives rise to benzoic acid and glycine (or sugar of

gelatine). The greater proportion of the former body is lost by evaporation: the latter may be readily detected by adding to the cold liquid a drop or two of a solution of sulphate of copper, and then an excess of caustic potash, when a deep blue-coloured liquid will be produced, which will not deposit a red precipitate on boiling.

### 10.

**COLOURING MATTERS.**—Our acquaintance with the colouring matters of urine is very imperfect. If a little healthy urine be boiled in a test-tube with about one-fourth of its bulk of hydrochloric acid, a deep brownish-purple colour will be produced. This discoloration is due to the presence of a peculiar highly carbonised pink colouring matter, known by the name of *purpurine*. The yellow colour of urine is probably caused by some other pigment. The common pink deposits of urate of ammonia owe their colour to purpurine, which has a great tendency to become thus precipitated with the urates. If perfectly white urate of ammonia (boa's excrement) be boiled in urine containing a large amount of purpurine, on cooling the urate will be deposited of a pink colour, in consequence of its carrying down the purpurine with it. If these deposits, natural or artificial, be boiled in alcohol, the purpurine will be dissolved, forming a pinkish-red solution.

### 11.

**EXTRACTIVES.**—The remaining organic constituents of urine are called by this name. The extractives generally amount to about one per cent. of the urine. Included among the extractive we have some principle containing *sulphur* in an unoxidised form, also kreatine and kreatinine—substances derived from the oxidation of muscle, and found more largely in the juice of flesh.

### 12.

**INORGANIC CONSTITUENTS.**—The ashes of urine may be examined according to the directions previously given for the analysis of animal ashes. There will be found carbonic,

sulphuric, and phosphoric acids, chlorine, lime, magnesia, soda, and a small quantity of potash. After the ash has been acted upon by acid, a residue will be left consisting principally of carbon. If this residue be ignited for some time, a minute white ash will be left, which is said to contain silica and fluorine. Most of the inorganic constituents of the urine may be detected in the secretion itself after simple filtration. By the addition of ammonia a white precipitate will be produced. This, when examined microscopically, will be seen to consist of amorphous granules of *phosphate of lime* and characteristic stellate feathery crystals of *ammonio-phosphate of magnesia*. If urine, especially that passed after a night's rest, be evaporated very gradually upon a glass slide, minute octahedral crystals of *chloride of sodium* may be detected by microscopic examination. Generally speaking, however, the common salt is seen in the form of very complex right-angled crosslets (stauroid crystals), arranged somewhat like *chevaux de frise*. On the axes and extremities of these forms, octahedra may usually be recognised by a good defining glass.

Sulphuric and hydrochloric acids may be detected in the urine by the usual tests.

## ABNORMAL URINE.

The abnormal constituents of urine which do not necessarily give rise to deposits, are albumen, sugar, bile, and fat.

### 1.

**ALBUMINOUS URINE.**—The general appearances of albuminous urine are very variable. Sometimes it presents the usual characters of normal urine. The amount of flocculent deposit formed by repose is often larger in amount than that of the healthy secretion ; occasionally the urine has a faintly opalescent appearance, not removable by filtration ; very frequently it is met with, black, brown, or red, from the

presence of altered blood, with or without the occurrence of a deposit of blood globules: albuminous urine when shaken retains the froth for a long time. The specific gravity is very variable.

## 2.

**TEST BY BOILING.**—Boil a little of the suspected urine in a test-tube: should albumen be present, a turbidity will be produced, the amount of which may vary from a faint cloud to a bulky precipitate rendering the urine nearly solid. *Impediments.*— $\alpha$ . Albumen when dissolved in alkaline fluids is not necessarily deposited upon boiling, the formation or non-formation of a precipitate having reference to the quantities of albumen and alkali respectively present. Therefore, in testing an alkaline urine for albumen, render the liquid *very faintly* acid with acetic acid.  $\beta$ . A previously opaque condition of the urine interferes with the action of this test. This interference may be lessened, if not removed, by filtering the urine before applying the heat. In urine containing deposits, the clear liquid can generally be poured off and tested. Deposits of urates do not impede the action of this test, as, upon heating the urine, solution of the urates takes place before the precipitation of albumen.— $\gamma$ . Albuminous urine, to which a very minute quantity of nitric acid has been added, is not rendered turbid by heat. *Fallacy.* A precipitate of the earthly phosphates occasionally takes place, upon boiling certain varieties of urine. The deposit of albumen can be distinguished from that of the earthly phosphates, by the addition of a little dilute nitric acid, when the latter will be dissolved, the former unaffected.

## 3.

**NITRIC ACID TEST.**—On adding nitric acid to albuminous urine a white turbidity is produced, varying in amount with the amount of albumen present. *Impediments.*— $\alpha$ . The reagent should be added drop by drop, since a minute quantity does not cause any precipitate, and a very great excess dissolves any precipitate which may be formed.  $\beta$ .

When the urine is opaque, it should be rendered alkaline with potash, agitated, filtered, and then tested with the acid.

*Fallacies.*—*a.* In some varieties of urine the addition of nitric acid produces a precipitate of uric acid. This precipitate, however, speedily shrinks very much in bulk, and when examined microscopically is seen to be crystalline, whilst the deposit of albumen is amorphous. *β.* Nitric acid produces a whitish turbidity in the urine of patients who have been taking copaiva, cubebs, and probably other oleo- and resinous medicines. The precipitate of albumen subsides to the bottom of the test-tube in the course of a few hours; the precipitate of oleo-resinous matters remains suspended in the urine for two or three days. Moreover, inquiry can always be made on these points.

## 3.

**FERROCYANIDE OF POTASSIUM TEST.**—If ferrocyanide of potassium be added to urine previously acidulated with acetic acid, a white precipitate is produced. *Impediment.*—The addition of acetic acid to urine occasionally produces a precipitation of mucus: under these circumstances the acidulated urine must be filtered before adding the ferrocyanide.

## 4.

**SACCHARINE URINE** cannot be distinguished by the eye from the normal secretion. It generally has a high specific gravity, a somewhat fragrant odour, and when agitated retains its froth for some time. It is said to have a distinctly sweet taste.

## 5.

☞ **POTASH TEST.**—To the suspected urine, an equal bulk of the ordinary solution of caustic potash is to be added, and the whole boiled: a deep orange-brown, frequently almost black, colour will be produced if sugar be present.

*Fallacies.*—Should a dark brandy colour be produced the test is free from fallacy. There are many specimens of non-saccharine urine, however, which when boiled with caustic potash acquire a tolerably dark sherry colour. Moreover,

caustic potash frequently contains lead, and this impure reagent, acting upon the sulphur of ordinary urine, or more markedly in albuminous specimens, will give rise to a brown discolouration. The potash should therefore be first tested for lead.

### 6.

• **COPPER TEST.**—The urine is to be mixed with about half its bulk of caustic potash solution : a precipitation of earthy phosphates will be produced. In questionable cases this precipitate should be separated by filtration. To the alkaline liquid, filtered or unfiltered, a drop or two of a diluted solution of sulphate of copper is to be added : a greenish or bluish precipitate will be produced, which, if sugar be present, will disappear upon agitation, forming a deep blue-coloured liquid. Upon heating this liquid, and even before it arrives at the boiling point, a red or orange-coloured precipitate will be produced, characteristic of sugar. **Fallacies.**—Although the precipitate produced by the addition of sulphate of copper to a mixture of normal urine and caustic potash does not disappear upon agitation, still the formation of the blue solution is no proof of the presence of sugar. Moreover, the application of heat should not be continued after the liquid has acquired a boiling temperature, as many substances by prolonged ebullition effect a deposition of the red suboxide of copper.

### 7.

**FERMENTATION TEST.**—Ordinary yeast, or the dried German yeast, is to be mixed with water ; and a test-tube is then to be completely filled with the suspected urine, to which a little of the yeast liquid has been added. The tube is to be closed with the thumb, and inverted in a saucer containing a little of the urine under examination, so that no air may enter the tube ; the whole is then to be set aside in a tolerably warm situation. The temperature should not be below 70° Fahrenheit. If the urine be saccharine, minute air-bubbles will speedily make their appearance, and in the course of an hour or so a very definite quantity of gas should occupy the upper part of the tube.

## 8.

BILIARY URINE has a yellowish-brown colour, and a persistent bitter taste. According to the experience of the best observers, the urine as voided never contains the true biliary salts, for the detection of which substances only is Pettenkofer's test adapted. Heller's test, and the nitric acid test, react upon the colouring matter of bile, which not unfrequently finds its way into the urine.

## 9.

PETTENKOFER'S TEST.—For practice, this reaction may be performed with urine to which a small quantity of bile has been purposely added, and for a negative result in urine containing the colouring matter of bile. To a little of the urine in a test-tube add half its bulk of strong sulphuric acid : the addition must be made very gradually, and the tube kept perfectly cool by immersion in water : now add a minute quantity of powdered white sugar, agitate the mixture, and drop into it more sulphuric acid. By this means the temperature will gradually rise to the requisite point, and a deep purplish crimson colour be produced in the specimen to which bile had been added. A somewhat similar reaction may be produced in albuminous urine.

## 10.

HELLER'S TEST.—For the application of this test the urine must contain albumen ; therefore, if necessary, add a little diluted white of egg, serum of blood, or some other urine containing albumen. Then add nitric acid : if bile be present the precipitate will have a distinctly bluish or greenish colour.

## 11.

NITRIC ACID TEST.—Pour a little of the urine, previously concentrated if necessary, upon a white plate, so as to form a thin layer ; then let fall a drop or two of strong nitric acid. Where the acid comes into contact with the biliary urine, a peculiar play of colours will be observed,—green, pink, violet, and yellow, being readily recognised.

## 12.

**FATTY URINE.**—The conditions in which fat occurs in the urine have not been ascertained with any degree of precision.  $\alpha$ . Occasionally, in examining the ordinary flocculent deposit of urine by means of the microscope, isolated fat globules may be recognised. Fat occurring in this state only is believed by some observers to be necessarily of extraneous origin.  $\beta$ . In some forms of Bright's Disease the fibrinous casts of tubes, and the epithelial cells, particularly those derived from the kidney, may be seen loaded with fat, and at the same time isolated fat globules may be detected.  $\gamma$ . Occasionally the so-called chylous urine is met with ; the secretion is more or less opaque, always contains albumen, frequently gelatinises on cooling, and when examined microscopically displays an abundance of minutely divided granular matter, a few granular cells similar to those found in the chyle, but no fat globules. Fat, however, may be readily obtained by agitating the urine with ether, and evaporating the ethereal residue.  $\delta$ . In the urine of pregnant women the so-called kiestein may be recognised. The secretion has generally an acid reaction, and by repose becomes faintly opaque. In the course of two or three days a fat-like scum rises to the surface, remains there for two or three days, and then sinks to the bottom of the vessel, the urine becoming at the same time ammoniacal. If this scum be examined microscopically, it will be seen to consist of crystals of triple phosphate, with a few fat globules, imbedded in a dense granular matter. This granular matter appears to be of an albuminous character, containing, however, minutely divided fat. Kiestein urine, by keeping, frequently evolves a powerful odour of putrescent cheese.

## URINARY DEPOSITS.

These may be distinguished from one another by attention to the following characters :—

## 1.

A FLOCCULENT DEPOSIT, varying slightly in its quantity and appearance, separates from urine by repose. This deposit is not indicative of disease: its characters have been before alluded to. It should, however, be examined microscopically, since in addition to the normal mucus corpuscles, and epithelium scales, there may be present torulæ characteristic of saccharine urine, casts of uriniferous tubes indicative of Bright's disease, fat globules, whether free or contained in a cell wall, vibriones, spermatozoa, blood globules, exudation globules, minute crystals of oxalate of lime, and occasionally of uric acid, &c. &c.

## 2.

URATES OR LITHATES.—*Every deposit which disappears upon the application of heat, consists of uric acid united to bases, principally soda and ammonia.* These alkaline urates are sometimes white, but generally more or less coloured with purpurine, which colouring matter may be partially extracted by means of hot alcohol. They form a bulky deposit, nearly always amorphous, occasionally appearing in the form of minute spheres with protruding spiculæ. These sediments dissolve readily on the addition of caustic potash, the solution when boiled giving off ammonia. Moreover, they yield a residue of murexid, when treated with strong nitric acid, evaporated to dryness, and held over the vapour of ammonia. The urine in which these deposits occur has generally an acid reaction.

## 3.

EARTHY PHOSPHATES.—*Nearly every deposit which disappears upon the addition of hydrochloric acid consists of the earthy phosphates.* The earthy phosphates form a bulky opaque white deposit, which, unless associated with mucus, is easily diffusible upon agitation. The urine itself is generally alkaline, neutral, or very faintly acid. The phosphate of lime is amorphous; the ammonio-phosphate of magnesia crystallises in four-sided prisms, often simulating irregular

six-sided plates, and in very ammoniacal urine is met with in the form of stellate feathery crystals. In acid urine, where the magnesian salt preponderates, the precipitate may be met with dense and obviously crystalline. In some cases this deposit is seen as an iridescent pellicle, and occasionally it remains for a long time suspended in the urine.

#### 4.

**URIC ACID.**—*Every obviously crystalline deposit, having a distinctly yellow or red colour, consists of uric acid.* The crystalline forms of uric acid are very variable (*vide page 77*). The colour, specific gravity, and acidity of the urine, are generally rather above than below the average. The precipitate is compact in its appearance, and readily soluble in potash, from which solution it is reprecipitated on the addition of hydrochloric acid. When treated with strong nitric acid, evaporated to dryness, and held over the vapour of ammonia, it yields murexid: uric acid deposits are very rarely indeed devoid of colour.

#### 5.

**OXALATE OF LIME** rarely if ever forms a distinct sediment. It may be detected by allowing the urine to stand at rest for some time, and then pouring away all but the last portions, which must be examined microscopically. Oxalate of lime occurs in well-marked octahedra, the crystals generally appearing to have a square outline, and the opposite angles being connected by markings. The sediment may be rendered apparent to the naked eye, by warming the lowest stratum of the urine, giving it a rotatory motion, and allowing it to stand for a few minutes; then, on pouring off the urine, and replacing it by water, a white glistening deposit will be apparent. This deposit of oxalate of lime is scarcely at all affected by cold potash. It dissolves without effervescence in hydrochloric acid; by ignition it leaves a residue of carbonate of lime, which dissolves in the acid with effervescence. There are occasionally found associated with the octahedra of oxalate of lime, certain dumb-bell shaped crystals, said to consist of oxalurate of lime. They are insoluble in potash,

soluble in hot hydrochloric acid, and when incinerated leave a residue of carbonate of lime.

### 6.

CYSTINE occurs somewhat rarely. It forms a bulky, easily diffusible deposit, resembling in its appearance the white or pale lithates. When examined microscopically it is seen to consist of more or less distinct six-sided plates, variously superimposed one upon the other. The centre portions of the crystals are usually somewhat opaque. If the supernatant urine be poured off, the sediment will be found to be insoluble in acetic acid, soluble in hydrochloric acid, very soluble in ammonia. If the ammoniacal solution be allowed to evaporate spontaneously on a slide, very well-defined, transparent hexagonal plates crystallise out. Cystine is remarkable for containing twenty-six per cent. of sulphur. If cystic urine be boiled, with a solution of acetate of lead to which potash has been added in sufficient excess to dissolve the precipitate at first thrown down, the whole will become nearly black, from the formation of sulphide of lead. Cystic urine has when recent an aromatic, when decomposing a very foetid odour.

### 7.

Pus presents a different appearance accordingly as it occurs in acid or alkaline urine. In acid urine, purulent deposits sink to the bottom of the vessel, form a greenish yellow opaque layer, having a creamy consistency, an easy diffusibility on agitation, and a slow subsideney on repose, gelatinising when agitated with an equal bulk of caustic potash, and in fact presenting all the ordinary qualities, physical and microscopical, of pus. In alkaline urine the deposit is viscid, tenacious, ropy, and not diffusible on agitation. It is mixed up with the earthy phosphates, which may, however, be separated by the action of dilute hydrochloric acid. Purulent urine is necessarily albuminous. If the deposit be agitated with ether, and the ether poured

off and evaporated, a considerable residue of oily globules will remain.

The pus corpuscles (which, however, can be scarcely said to exist after the action of an alkali) consist of circular granulated cells, somewhat larger than blood globules. When acted upon by acetic acid, they swell very considerably, the margins become distinct, and two, three, or four little granular masses are seen in the centres.

### 8.

MUCUS is always met with even in normal urine; it may be much increased in amount, but scarcely altered in its character. Sometimes it is met with in the form of gelatinous masses, which sink to the bottom of the vessel, or, from the entanglement of air-bubbles, remain for a long time suspended in the secretion.

Mucus deposits have a more or less marked alkaline reaction, even when the supernatant urine is acid: they do not diffuse readily by agitation, and are frequently associated with a very considerable sediment of the earthy phosphates. The presence of even a large amount of mucus does not of itself render the urine albuminous. The microscopical characters of the mucus corpuscle are very similar to those of the pus corpuscle. The granular character is perhaps not quite so well marked.

### 9.

BLOOD.—Urine containing blood is necessarily albuminous. By allowing the urine to stand, and examining the sediment microscopically, blood globules may be recognised by their uniform size, their non-granular surface, and their yellow colour. The appearance of urine containing blood is very variable: the colour may be light-red, dark-red, reddish-brown, smoke-brown, or scarcely altered. The sediment also varies much in its colour: sometimes its nature is apparent to the unassisted eye, sometimes it occurs in very minute quantities, and can only be identified microscopically. Urine

may contain altered colouring matter of blood, and yet the blood-corpuscles escape detection.

## CLINICAL EXAMINATION OF URINE.

### 1.

**APPEARANCE, &c.**—It is advisable to notice the colour; whether pale from a dilute urine, or dark from a concentrated urine or from excess of purpurine, whether yellowish brown from bile, or red or brown from blood—the taste, whether sweet from sugar, or bitter from bile—the smell, whether fragrant from cystine or from sugar, or foetid from alkalinity, with or without mucus, or from cystine—any opalescence or milkiness due to fat, kiestein, mucus, or a modification of albumen, &c.

### 2.

**SPECIFIC GRAVITY.**—The specific gravity should be taken by means of a gravimeter. It may be too low, from an accidentally diluted urine, or from *Diabetes insipidus*, or from certain forms of *Morbus Brightii*, &c.; too high, from a concentrated urine, or from the presence of sugar, &c. Dr. Bird has pointed out the very curious coincidence, that the last two figures, expressing the specific gravity, represent very nearly the number of grains of solid matter contained in an ounce of the secretion: thus in urine of the specific gravity 1017 every fluid ounce contains about 17 grains of solid matter.

### 3.

**QUANTITY.**—In order to determine the quantity of urine passed in twenty-four hours, the patient should be made to make water at some definite hour in the day,—say 10 A.M., the amount then voided being neglected. After this he must save all the urine he passes until 10 o'clock on the next day, at which time he must again empty his bladder, and add the contents to the specimen to be measured. The patient should moreover be desired always to micturate before going to the closet. By multiplying the number of ounces

passed, by the last two figures of the specific gravity, an approximation will be arrived at as to the total amount of solids excreted by the kidneys in twenty-four hours.

4.

**REACTION TO TEST-PAPER.**—Normal urine has a slightly acid reaction. If the urine be alkaline, it will restore the blue colour of reddened litmus-paper. Should the blue colour remain after the paper has become dry, the alkalinity is due to the presence of a fixed alkaline salt; should the red colour disappear on drying the paper, the alkalinity is due to ammonia.

5.

**EXAMINATION OF THE URINE.**—The supernatant urine should be poured away from any deposit which may have formed, and should be examined for albumen, sugar, purpurine, and if necessary fat and bile. Should the urine have a high specific gravity and be free from sugar, it may be examined for an excess of urea as follows:—Pour a little of the urine into a watch-glass, and add about two-thirds its bulk of cold concentrated nitric acid. The formation of a crystalline deposit of nitrate of urea is, with certain restrictions, indicative of an excess of that base. It is, perhaps, generally advisable to concentrate the urine slightly, before adding the acid.

6.

**EXAMINATION OF THE DEPOSIT.**—The appearance of the deposit generally indicates the order in which the tests, both microscopical and chemical, should be applied. The lithates are dissolved by heat, dissolved by potash, dissolved by hydrochloric acid; the phosphates are undissolved by heat, undissolved by potash, dissolved by hydrochloric acid; uric acid is undissolved by heat, dissolved by potash, undissolved by hydrochloric acid; cystine is undissolved by heat, dissolved by ammonia or potash, dissolved by hydrochloric acid; oxalate of lime is undissolved by heat, undissolved by potash, dissolved by hydrochloric acid. In mixed deposits

the different ingredients are readily recognised by their different microscopical appearances, and by their different behaviour with the above reagents.

### URINARY CALCULI.

Urinary calculi are for the most part constructed of concentric layers. This structural arrangement can be readily seen by making a section of a calculus through its centre. All the layers of a calculus may have the same composition, or they may differ very much from one another in this respect. One single uniform layer of a calculus may be, and generally is, composed of several ingredients.

It is probable, that if a very exact analysis were made, each of the layers of nearly every calculus would be found to contain uric acid, alkaline urates, phosphate of lime, and ammonio-phosphate of magnesia, with or without the other constituents of calculi. Moreover, most calculi contain traces of all the salts naturally existing in the urine, as well as colouring matter, mucus, &c.

From these considerations it is obvious that the chemical examination of a calculus need only have reference to its general composition, and not to its exact analysis. It is important, however, to bear in mind, that even a homogeneous layer of a calculus rarely ever consists of one constituent only.

The general appearances, &c. of the different varieties of calculi are as follows :—*a. Uric calculi* consist of uric acid, with or without variable proportions of the alkaline urates : usually they have an uniform outline, a compact laminated structure, and an orange or yellow colour ; sometimes the laminated appearance is wanting, and sometimes they have a light fawn colour, resembling the paler varieties of oxalate of lime concretions. A greater or less amount of uric acid is found in the centres of most calculi. *β. Earthy phosphates* consist of phosphate of lime and ammonio-phosphate of magnesia. It rarely if ever happens that where one of these

constituents is present the other is wholly absent. When the two exist in about equal quantities, the concretion is known by the name of the *fusible calculus*, in consequence of the readiness with which it fuses in the blow-pipe flame. When either of the constituents is present in great excess, this fusion cannot be effected. The distinctly laminated character appears to be more frequently wanting in the fusible than in most other varieties of calculi. Phosphatic calculi differ much in their appearance; they have usually a smooth uniform surface, and a pale, white, or even chalk-like aspect. Sometimes they are compact and hard, at other times light and friable; sometimes the layers adhere very closely to one another, and at other times they are just as easily separable. The earthly phosphates may constitute the greater part of a calculus, or may be disseminated through the other constituents, or may form distinct layers; they give a more or less thick external coating to most calculi.

$\gamma$ . *Oxalate of lime* calculi are generally recognised by their dark colour, hard compact structure, and irregular surface. The term mulberry calculus does not give any idea of the degree of this irregularity. Some small oxalate of lime calculi, known as hemp-seed concretions, have a smooth contour. Occasionally the oxalate of lime concretions, especially when forming layers in other calculi, or when mixed with uric or phosphatic deposits, have a pale colour, and a very finely laminated structure. The central portions of oxalate of lime calculi generally contain more or less uric acid.

$\delta$ . *Cystine* calculi are of comparatively rare occurrence. They have an irregular shape, a rough and crystalline-looking surface, a fawn-brown colour when recent, and a sea-green colour when long kept. Cystine rarely ever enters into the constitution of composite calculi.

Some of the ingredients of calculi are destructible by heat, some indestructible, as seen in the following table :—

Destructible.	URIC ACID.
	URATE OF AMMONIA.
	CYSTINE.
	OXALIC ACID, from oxalate of lime.
	AMMONIA, from triple phosphate.
Indestructible.	URIC ACID, from urates of lime and soda.
	PHOSPHATE OF LIME.
	CARBONATE OF LIME.
	PHOSPHATE OF MAGNEŚIA, from triple phosphate.
	CARBONATE OF SODA, from urate of soda.
	CARBONATE OF LIME, from oxalate and urate of lime.

*Note.*—If the heat be sufficiently prolonged and intense, the carbonate of lime will become converted into caustic lime. Carbonate of lime is not an unfrequent constituent of calculi which have undergone partial decomposition in the bladder.

#### ANALYSIS OF CALCULI.

##### 1.

PULVERISATION, &c.—The calculus to be examined should be sawn through its centre, so as to expose its internal arrangement. Should it consist of layers obviously differing from one another, each of them should be separately examined. For this purpose, a sufficient quantity of each layer may be consecutively removed by means of a pocket-knife. The determination of the nature of any one layer should be ascertained before removing a specimen of the next one. In friable calculi, great care must be exercised in obtaining specimens of the different layers. The smooth appearance of the flat surface can be readily restored by grinding, so that a calculus may be analysed without any necessary disfigurement. The specimen removed from the calculus is to be reduced to a fine powder.

##### 2.

IGNITION.—Heat a little of the powder upon platinum foil, and notice which of the following conditions occur:—

a. *Charring*.—All urinary calculi undergo a slight amount of charring. In oxalate of lime calculi this is very slight, and speedily disappears, leaving a bulky white pulverulent residue. In phosphatic calculi the charring is more complete, and the carbon not so easily burnt off.

β. *Decrepitation*.—This is always very slight: when occurring simultaneously with the formation of a white smoke and a great degree of mobility in the heated powder, it is indicative of urate of ammonia.

γ. *Odour*.—Oxalate of lime calculi do not evolve much odour when heated: most others do. The odour produced by the ignition of cystine is very powerful and characteristic.

δ. *Volatilization*.—Should the calculus powder burn away almost entirely, it will suffice to test for uric acid, urate of aminonia, and cystine.

ε. *Fusion*.—The heat of a spirit-lamp is frequently sufficient to fuse the mixed earthy phosphates.

ζ. *Alkalinity*.—Moisten the residue with water, and apply a piece of rose-paper: if the heat of the lamp only has been employed, any alkalinity is probably due to carbonate of soda derived from the ignition of ~~carbonate~~<sup>lime</sup> of soda.

η. *Effervescence*.—To the residue moistened with water add a drop or two of nitric acid. Effervescence denotes the presence of a carbonate, whether originally existing as such, or derived from the ignition of the oxalate of lime or of the fixed alkaline urates; in which latter case the amount of effervescence is usually very small.

θ. *Blow-pipe*.—Should the ordinary flame have proved incapable of fusing the ash, the moist residue may now be dried, and strongly heated in the blow-pipe flame; when, if the mixed earthy phosphates be present, a more or less complete fusion, or at any rate cohesion of the particles, will take place.

ι. *Phosphoric Acid*.—Place the foil upon a watch-glass, and again moisten the residue with water and nitric acid: any carbonate of lime will probably have become converted into caustic lime, so that effervescence will rarely manifest itself.

Add a few drops of nitrate of silver, and carefully neutralise the liquid thus produced with dilute ammonia. The production of a yellow precipitate will be indicative of the presence of phosphoric acid. Under certain circumstances, especially when the triple phosphate constitutes the great mass of the calculus, or when the silver salt has been added in very small quantity, the precipitate will be white.

### 3.

**AQUEOUS SOLUTION.**—Put some of the powdered calculus into a test-tube, and boil it for a few minutes with a little distilled water; then throw the whole upon a filter, collect the filtrate, (A) and wash the residue thoroughly with boiling water. The first portions of the washing may be reserved for use on an emergency.

This aqueous solution A may contain

URATE OF AMMONIA.

URATE OF SODA.

URATE OF LIME.

### 4.

**HYDROCHLORIC SOLUTION.**—Boil the well-washed residue for some time in dilute hydrochloric acid; observe whether any effervescence, indicative of the presence of carbonate of lime, takes place, and throw the whole on to a filter. Collect the filtrate (B) and wash the residue (C) thoroughly with water.

The hydrochloric solution B may contain

CARBONATE OF LIME.

OXALATE OF LIME.

CYSTINE.

PHOSPHATE OF LIME.

AMMONIO-PHOSPHATE OF MAGNESIA.

The residue C will consist of

URIC ACID.

### 5.

**EXAMINATION OF AQUEOUS SOLUTION A.**—Evaporate a few drops of the solution upon a glass plate: should but a mere trace of residue be left, the liquid may be disregarded,

and the calculus considered as free from any appreciable amount of the alkaline urates. Should, however, an obvious residue be left, pour about a quarter of the solution A into a test-tube, and boil it with an equal volume of caustic potash. By this treatment *ammonia* if present will be given off, and may be recognised by its odour, by its action on test paper, and by its forming white vapours when held near a glass rod moistened with hydrochloric acid. Evaporate the remainder of the solution A to a small bulk, then add about an equal quantity of strong nitric acid, and evaporate cautiously to dryness in a small capsule. A pinkish residue, which when held over the vapour of ammonia assumes a crimson colour, will be indicative of *uric acid*. Incinerate the contents of the capsule, and should there be any residue add a few drops of water, and divide the liquid, clear or turbid, into two portions. To one add a drop of acetic acid, and then a drop of oxalate of ammonia—the production of a white turbidity will indicate the presence of *lime*; to the other add a drop of hydrochloric acid and evaporate cautiously to dryness—the production of cubical crystals will indicate the presence of *soda*.

## 6.

**EXAMINATION OF HYDROCHLORIC SOLUTION B.**—Render the solution, by means of dilute ammonia, as neutral as it can possibly be rendered, without having its transparency affected, and then add acetate of ammonia; the production of a white precipitate will denote the presence of *oxalate of lime* or *cystine*. The latter body rarely occurs in mixed calculi, and could be readily separated from the oxalate of lime by dissolving it in ammonia. By evaporation of the ammoniacal solution it would be deposited in the form of hexagonal tablets. To the clear liquid if no precipitate has occurred, or otherwise to the filtrate therefrom, add oxalate of ammonia in excess; the deposition of a white precipitate will indicate the presence of *lime* which did not previously exist in combination with oxalic acid. Filter if necessary, and to the clear liquid add ammonia in excess, and stir for some time: the production of a

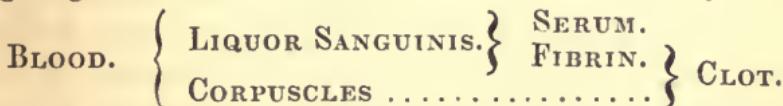
white crystalline precipitate will prove the presence of *phosphoric acid* and of *magnesia*. Should there be no obvious precipitate, add sulphate of magnesia, and stir; the presence of *phosphoric acid* will be indicated by the formation of a white crystalline precipitate.

## 7.

**EXAMINATION OF THE RESIDUE C.**—Treat the residue with concentrated nitric acid, and evaporate to dryness; a pink mass will be left, which when held over the vapour of ammonia will become crimson, and if subsequently moistened with potash will become purple,—reactions characterising *uric acid*.

## BLOOD.

Blood as existing in the vessels is seen to consist of *red corpuscles* floating in a clear liquid, termed the *liquor sanguinis*. Blood when removed from the vessels speedily separates into two portions,—a clear yellow liquid, the *serum*, and a solid red mass, the *clot*. The liquor sanguinis consists of fibrin and serum; the clot, of fibrin and corpuscles, as seen in the following diagram :—



Thus the chemical investigation of the blood naturally divides itself into separate examinations of the clot and serum.

**EXAMINATION OF THE CLOT.**

## 1.

**COAGULATION.**—The coagulation of the blood is due to the solidification of fibrin, which entangles in its meshes the corpuscles and a considerable portion of the serum, so as to form a firm jelly-like mass. While the blood is circulating through the vessels of living animals, the fibrin exists in a state of perfect solution. The circumstances which determine

this state of solution are not well understood ; intimate contact with the living tissues appears to be one very important condition. Out of the body the fibrin speedily solidifies, the coagulation being generally complete in about ten minutes time. Variations of temperature, movement, and exposure to air, modify but never prevent the coagulation. If the blood be rapidly frozen, and even retained for some time in the solid state, it will on thawing speedily coagulate. When the fibrin exists in large quantity, the coagulation takes place more slowly, but the coagulum is firmer and more compact. If blood be removed from persons suffering from any inflammatory condition of system, or if it contain an excess of fibrin, or a deficiency of corpuscles, or if it be collected in a deep narrow vessel, or if its coagulation be retarded by any means, the corpuscles sinking before the coagulation is complete, exist principally in the lower portion of the clot, while the upper layer consists of nearly colourless fibrin. This colourless layer is termed the *buffy coat* ; it is extremely tenacious, and frequently by its slow contraction draws up the edges of the clot, so as to form a cup-like depression.

## 2.

**FIBRIN FROM UNCOAGULATED BLOOD.**—Fibrin is most easily procured from this source. The blood, before it has had time to coagulate, must be rapidly whipped with a few twigs of wood, or it may be well shaken in a bottle with two or three irregular pieces of lead. In this way the fibrin separates more or less completely from the corpuscles, and adheres to the twigs or pieces of lead in the form of loose fibrous masses. These are to be well washed with water, and also with ether if it be required to remove the adherent fat.

## 3.

**FIBRIN FROM THE CLOT.**—The preparation of fibrin from coagulated blood is rather more tedious. The clot should be placed upon a cloth thoroughly broken up by the hand, and washed under a stream of water : by alternately washing and

kneading the clot, the serum and colouring matter will pass through the cloth, and a residue of tolerable white fibrin be left thereon.

## 4.

**PROPERTIES OF FIBRIN.**—Fibrin possesses all the chemical properties of coagulated albumen (*vide p.103.*) When examined microscopically it is seen to differ from coagulated albumen in manifesting an organised structure, though of the lowest type, viz., the simply fibrous. The fibrillated arrangement is best seen in the buffy layer of inflammatory blood. If moist fibrin, especially that obtained from the clot, be covered with water rendered *faintly* alkaline by soda, and be left at rest for some days in a tolerably warm situation, the greater part of it will dissolve, and in the filtered liquid albumen may be detected by the action of heat and nitric acid. Fibrin constitutes about 0·25 per cent. of normal blood.

## 5.

**APPEARANCE OF THE CORPUSCLES.**—If a drop of uncoagulated blood, or a drop of the deep red-coloured serum squeezed out of the clot, be examined under a good quarter-inch object glass, with a high eye-piece, the field of the microscope will be covered with minute coloured cells, of uniform size, circular outline, and non-granular structure. According to the focussing the edges will appear dark and the centre transparent, or *vice versa*. Some of the globules may be seen lying upon their edges, some of them adhering to one another by their flat surfaces, forming rouleaus. In the case of the previously uncoagulated blood, a delicate net-work of fibrin will speedily appear. Blood corpuscles appear to consist of a transparent membrane containing a red-coloured fluid. The phenomena of *osmose* may be readily seen under the microscope : if a concentrated solution of sulphate of soda be added, the corpuscles become distorted, the edges uneven, and the dark centres seem to occupy a greater extent ; if, however, water be added, the corpuscles swell up, the dark centre and defined

margin gradually disappear, and finally the cells burst with discharge of their contents.

In addition to the above-described red corpuscles, there may generally be seen a few of the colourless corpuscles. In healthy blood these are said to exist in the proportion of about 1 to 50 of the red, than which they are rather larger in size, and more irregular in outline. Moreover, they manifest a faintly granular structure.

### 6.

**BLOOD CRYSTALS.**—The formation of these crystals was first discovered by Dr. Otto Funke, of Leipsic. It appears that by the bursting of the red corpuscles as above described, an aqueous solution of the colouring matter is obtained, which by very slow evaporation of the liquid gives rise to crystals having very definite forms. The blood of some of the lower animals, particularly the rodentia, yields crystals more readily than that of man; from which latter source, however, they may be procured as follows:—Take a portion of clot which is one or two days old, squeeze a drop or two of the deeply-coloured serum on to a slide, add about an equal bulk of distilled water. Cover the whole loosely with a piece of microscopic glass, and set aside in a light but not too warm situation: in the course of some hours, flattened, red-coloured, prismatic crystals, will make their appearance.

### 7.

**SEPARATION OF THE CORPUSCLES.**—If blood as it is flowing be received into a saturated solution of sulphate of soda, all coagulation will be prevented, and by repose the corpuscles will form a bright scarlet layer at the bottom of the vessel. The supernatant fluid may be poured off, and the sediment collected in a filter, and washed with a solution of sulphate of soda. Or the red liquor, from which the fibrin has been removed by agitation, may be allowed to subside; or the clot may be broken up, well shaken with the serum, and the red fluid thus formed be allowed to subside. From

either of these fluids the corpuscles will be deposited more or less completely. The supernatant, tolerably pale serum, may then be poured away, and be replaced by a solution of sulphate of soda; the corpuscles will behave as in the first instance, and may be collected upon a filter and washed with sulphate of soda as before.

## 8.

**PROPERTIES OF THE COLOURING MATTER.**—Haematosine, or the red colouring matter of blood, is remarkable for the amount of iron which it contains. The ash of blood corpuscles yields full 30 per cent. of peroxide of iron. The presence of iron in any of the other tissues or fluids, with the exception of the chyle, appears to be due to an admixture of blood. It is possible to obtain a modified haematosine free from iron; but such an experiment does not prove anything. The chemical reactions of the colouring matter may be recognised by throwing the corpuscles, after having been well washed with sulphate of soda and drained, into a considerable excess of cold water, when the cell walls will burst by endosmosis, and the coloured contents of the cells dissolve in the water, forming a deep red solution, which by filtration may be made perfectly bright. This red colouring matter is unaffected by ammonia, and is entirely destroyed by ebullition, with the formation of a dirty-coloured coagulum, which dissolves in caustic potash with an indistinct greenish colour. *Vide Exp. 9.*

## 9

**BLOOD STAINS.**—These occasionally form important objects of medico-legal inquiry. The chemical evidence has reference to the colouring matter of the blood; the microscopical to the form of the globules. Recent blood stains are of a bright red colour; older stains of a reddish brown: when on linen or other stuffs, the fibre becomes more or less stiffened.

(a). *Chemical Examination.*—Supposing the stain to be on some stuff, cut off a strip of the stained portion, and suspend it by means of a thread in a test-tube containing a little distilled water. Gradually, streaks of colouring matter will be seen

descending from the stuff to the bottom of the tube, and there forming a layer, of a deep red colour if the stain be recent, or a reddish-brown if the stain be of an older date. If necessary, several of the stained strips may be thus successively treated in the same portion of water, until a sufficiently dark solution is obtained. Stains on knives and other articles are likewise to be treated with cold water, so as to obtain a solution of the colouring matter. To the red or reddish-brown solution a little dilute ammonia is to be added : the colour will be unaltered, or simply brightened, but not changed to a green or crimson. When the solution of the colouring matter is boiled, the colour is entirely destroyed, and a dirty brown precipitate produced. Every stain which forms a reddish solution with cold water, which solution is unaffected by dilute ammonia, but has its colour destroyed by ebullition, with the formation of a precipitate, must be due to blood.

(b). *Microscopical Examination.*—Place upon a glass slide a little of the stained fibre, or, if possible, a little of the dried stain scraped away from the article under examination, moisten it with a solution of sugar (syrup diluted with about twice its bulk of water) or of pure glycerine reduced to the sp. gr. of .1028 : after some time a red-coloured liquid will be obtained, which may be covered with a piece of microscopic glass, and examined with a good quarter-inch object-glass. Should the stain be due to blood, the corpuscles, with their characteristic appearances, may in this way be readily detected : should they appear shrivelled, the addition of a drop or two of water will cause them to expand.

#### EXAMINATION OF THE SERUM.

##### 1.

WATER, ETC.—The serum is a pale yellow, transparent, viscid fluid, having a specific gravity of about 1030, while that of blood averages about 1055. The serum has a faintly alkaline reaction, and consists of water holding in solution albumen, fat, certain ill-defined extractive matters, and inor-

ganic salts. If serum be evaporated to dryness in a water-bath, the aqueous portions are driven off, and a hard, nearly transparent, horny residue is left. Water constitutes about 80 per cent. of normal blood.

## 2.

**SEPARATION OF ALBUMEN.**—For this purpose, either of the following methods may be adopted :—(a). Put the serum into a small capsule, add an equal bulk of coarsely powdered crystals of sulphate of soda, and boil; coagulation will take place; throw the whole on to a filter; a perfectly clear and nearly colourless liquid, quite free from albumen, will rapidly pass through: this method is equally applicable to serum containing any amount of colouring matter, and even to the broken-up clot itself. (b). Render the serum neutral or *very faintly* acid with acetic acid, boil, and filter: by this means the whole of the albumen will coagulate in flakes, and remain on the filtering paper, while a clear liquid, termed the *serosity*, will readily pass through. This precipitate of albumen is to be washed with hot water, and dried in a water-bath; moreover, a minute amount of earthy salts may be removed by boiling it in dilute hydrochloric acid, as also a small proportion of fat by boiling in alcohol.

## 3.

**PROPERTIES OF ALBUMEN.**—Albumen, as it exists in the blood and other animal fluids, is in a state of solution, capable, however, of being coagulated by heat. The temperature at which coagulation takes place varies with the alkalinity of the fluid, and with the amount of albumen present. Serum of blood coagulates at the temperature of about 160° F. Albumen once coagulated cannot again be obtained in the form of a solution coagulable by heat. Normal blood contains on the average about 7 per cent. of dissolved albumen. Fibrin and coagulated albumen agree in the following characters: they are insoluble in water, alcohol, and ether; they are soluble in potash, from which solution they are reprecipitated by neutralisation with an acid. If to the potash solution acetic acid be added, the

albumen will be at first precipitated, but subsequently redissolved in the excess of acid. Moreover, coagulated albumen and fibrin are soluble, though with difficulty, in acetic acid. Albumen and fibrin dissolve in boiling hydrochloric acid, forming deep purple solutions.

If albumen or fibrin be heated upon platinum foil, a minute white ash, consisting principally of phosphate of lime, will remain. This proportion of earthy phosphate appears to be an integral constituent of albuminous principles. If dried albumen or fibrin be heated in a reduction tube, into the mouth of which there have been inserted a piece of red litmus and a piece of lead paper, the red litmus will become blue and the lead paper black ; reactions indicating respectively the presence of nitrogen and sulphur.

#### 4.

**FAT.**—The condition in which fat exists in the serum is not well understood. Some portion of the fat is precipitated with the albumen, the remainder being dissolved in the serosity. As a rule, serum is perfectly bright, and fat globules cannot be detected in it by microscopical examination ; yet the fat being soluble in ether, does not appear to be saponified. In order to extract the fat, pulverise the dried residue left by the evaporation of the serum upon the water-bath, and agitate the powder for some time, with three or four times its bulk of ether ; allow the whole to subside, and after some hours pour off the ether and evaporate it to dryness in a water-bath, when a small quantity of a yellow semi-solid fat will be left. This may be treated with cold alcohol, when an oily fat will be dissolved and a crystalline fat be left unacted upon.

#### 5.

**EXTRACTIVES AND ALKALINE SALTS.**—The serosity consists of an aqueous solution of certain ill-defined organic compounds, known as extractives, and of the usual alkaline salts. All the organic constituents of the serum, with the exception of the albumen and fat, receive the name of extractives. If the serosity be carefully evaporated almost to dryness, very

beautiful cubes of common salt crystallise out. Moreover, sulphuric and phosphoric acids can readily be detected; the former by the formation of a white precipitate with nitrate of baryta and nitric acid; the latter by the addition of sulphate of magnesia, ammonia, and chloride of ammonium, when on stirring a white crystalline precipitate will be produced. If the serosity be evaporated to dryness, and ignited, a white fusible ash will remain. This may be examined according to the directions for the analysis of animal ashes, and will be found to contain chlorine, carbonic, phosphoric, and sulphuric acids, soda, potash, and traces of lime.

## 6.

SERUM CONTAINING UREA.—It is probable that the blood always contains minute traces of urea: in certain forms of disease, particularly in Bright's disease, the amount of urea becomes very sensible. In order to detect it, remove the albumen from the serum by either of the methods described in Experiment 2, and evaporate the serosity carefully to dryness. If the process (*b*) be adopted, and in the dried residue the chloride of sodium be seen to crystallise in well-marked octahedra instead of cubes, the presence of urea is tolerably certain. Warm the dry residue with a little strong alcohol, filter, evaporate the alcoholic filtrate to dryness, and dissolve the residue in a very small quantity of distilled water: this solution must be filtered, and concentrated in a watch-glass. To the cold concentrated liquid, an equal bulk of cold colourless nitric acid is to be added, when, if urea be present, a crystalline deposit of nitrate of urea will be produced, which can be examined microscopically. The production of a crystalline deposit on the addition of nitric acid is in itself almost conclusive as to the presence of urea.

## 7.

SERUM CONTAINING BILE.—In jaundice, the serum of the blood is of a much darker yellow colour than usual, owing to the presence of biliary colouring matter, which may be identified as follows:—Add to the serum a little nitric acid; the albumen

will be precipitated of a bluish or greenish colour: or pour some of the serosity on to a plate, so as to form a thin layer of fluid, upon which let fall one or two drops of nitric acid, when a variable play of colours,—purple, yellow, and green,—will be produced.

## 8.

SERUM CONTAINING SUGAR.—Sugar exists abundantly in the blood, in cases of diabetes. Recent researches have moreover shown that the normal blood of the inferior cava, and of the right side of the heart, contains sugar in very definite amount. To detect it, remove the albumen from the blood by means of sulphate of soda, as in Experiment 2, and to the clear filtrate add a drop or two of a solution of sulphate of copper, and then an excess of caustic potash: a deep blue-coloured liquid will be produced, which, on the application of heat, will deposit a red or orange-yellow coloured precipitate of suboxide of copper.

## MISCELLANEOUS ANIMAL PRODUCTS.

## 1.

BILIARY CALCULI.—The reactions of bile have been described under the head of biliary urine. Concretions are occasionally formed in the gall-bladder, sometimes in very considerable numbers. The appearance presented by these calculi is very variable; usually they have flattened sides, are rather larger than peas, have a soapy feel, are of a fawn-yellow colour, and are easily crushed by pressure. They consist principally of *cholesterine* and an insoluble combination of *bile pigment with lime*. When rich in cholesterine, they float upon water. To detect the cholesterine, powder the calculus, boil the powder in alcohol, and filter; on cooling, delicate transparent plates will crystallise out of the yellow solution. These crystals, when examined microscopically, are seen to consist of delicate, nearly square, rhombic plates, superimposed one upon the other.

Cholesterine is soluble in ether and hot alcohol, very slightly soluble in cold alcohol, not at all soluble in water.

## 2.

GOUTY CONCRETIONS consist principally of *urate of soda* and *phosphate of lime*. The uric acid may be readily detected by acting upon the concretion with concentrated nitric acid, evaporating to dryness, and holding the residue over the vapour of ammonia, when the crimson colour of murexide will be developed. If the concretion be incinerated, phosphoric acid, lime, and soda, can be detected in the ash by the usual tests.

## 3.

MILK consists of *water* holding in solution *casein*, *lactine*, and *salts* holding in suspension an abundance of *fat globules*, to the presence of which the opaque white appearance of milk is due. The specific gravity of human milk averages about 1030. Normal milk has an alkaline reaction to test paper.

a. Fat globules may be easily recognised under the microscope: they are of various sizes, have well-defined dark margins, and appear to be surrounded by delicate cellular membranes, as they cannot be made to unite by pressure until after the addition of a little acetic acid. The milk secreted soon after delivery contains large, granular, fatty corpuscles, known as colostrum corpuscles. In milk abscess, &c. pus and blood globules may be occasionally detected.

b. Casein.—When ordinary or skimmed milk is evaporated, a scum forms on its surface, which, if removed, is soon replaced by a fresh one, and so on repeatedly. This property of forming a scum on evaporation was formerly considered peculiar to fluids containing casein. Casein differs from the other albuminous bodies in not being coagulable by heat, but being coagulated on the addition of a little very dilute acid, or by contact with decomposing animal membrane. Cheese is casein which has been precipitated by rennet, the dried decomposing lining membrane of the stomach of the calf. If skimmed milk be rendered slightly acid with acetic acid, and gently warmed, the casein will coagulate, and may be collected on a filter,

washed with hot water, and subsequently with hot alcchol : it will manifest all the usual properties of the albuminous bodies.

$\gamma$ . Lactine, or sugar of milk, may be readily detected in the whey which has been separated by filtration from the coagulated casein. Add a drop or two of sulphate of copper, and then an excess of potash : on boiling, a red precipitate of suboxide of copper will be produced. Sugar of milk does not readily undergo the alcoholic fermentation ; but by the action of putrefying curd becomes rapidly converted into lactic acid.

$\delta$ . The ash of milk contains the same constituents as most animal ashes ; the relative proportion of earthy phosphates is very large, and potash exists in it more largely than soda.

#### 4.

BONE consists principally of phosphate of lime, deposited in an animal basis. If a bone be soaked for some time in dilute hydrochloric acid, the earthy matter is dissolved out, and a flexible elastic mass, having the exact form of the original bone, is left unacted upon. This residue consists of gelatine, which by boiling dissolves in water, forming a solution which gelatinises on cooling : the solution is precipitated by tannic acid, but not by acetic acid nor by ferrocyanide of potassium. Pure gelatine does not contain sulphur. By the incineration of bone, the animal matter is burnt off, and a brittle, white, earthy residue, having the exact form of the original bone, remains. This earthy residue consists principally of phosphate of lime, with a little carbonate of lime and phosphate of magnesia, also minute quantities of fluoride of calcum ; which latter substance may be detected more readily, however, in fossil bones.

THE END.

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